Effect of spin polarisation on zigzag graphene nanoribbon functionalized with L-Phenylalanine -A DFT study

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Abstract: In our study, we have investigated the covalent functionalization of zigzag graphene nanoribbon (ZGNR) with the amino ($-NH_2$) group of aromatic amino acid L-Phenylalanine ($C_9H_{11}NO_2$) using the density functional theory (DFT) and local spin density approximation (LSDA) methods. The change in the electronic properties such as band gap, Fermi energy, kinetic energy, dipole moment, electron density, bond length and equilibrium geometry have been examined. We find that, the edge functionalization of spin polarized ZGNR using L-Phenylalanine (fZGNR) have a pronounced effect on tuning the bang gap for both the spin-up and spin-down channels, compared to the spin polarized bare ZGNR (bZGNR). Further, fZGNR at 300K creates a polar covalent bond which is confirmed through the partial charge transfer between ZGNR and L-Phenylalanine. The total energy and kinetic energy of bZGNR and fZGNR was calculated. Moreover, in order to get a better insight about the nature of the interactions, we also calculated the dipole moment of both the systems(bZGNR and fZGNR). Our findings predicts that, the fZGNR shows a high chemical reactivity, thereby offering an opportunity to use fZGNR for imaging and drug delivery applications.

Keywords: spin polarization, zigzag graphene nanoribbon L-Phenylalanine, DFT.

1. Introduction:

Growing research interest in the field of graphene raised the spirit to use carbon nanostructures for numerous applications[1]. Known to be the mother of nanostructures, graphene plays a vital role in materials science research due to its tunable physical[2] and chemical properties[3]. The sp^2 hybridized honey-comb structure of graphene makes it the strongest material[4,5] eventually a hundred times stronger than steel. Graphene's unique properties like chemical reactivity[6,7], Young's Modulus[8], large specific surface area[9], high intrinsic mobility[10] have been verified through various modeling studies and experiments. Theoretical studies have revealed that, the graphene's planar structure with least curvature has higher binding affinity compared to carbon nanotubes.[11] Further, the chemical modification of the graphene's surface through doping and functionalization helps to control its electronic properties.[12-15]

Graphene nanoribbons (GNRs) are quasi–one dimensional sp^2 structures of graphene constrained by their edges. GNRs, are strips of graphene with ultra-thin width (<50 nm). The electronic states of GNRs largely

depend on their edge structures (armchair or zigzag).[16,17] Density functional theory (DFT) and experimental studies have revealed that depending upon the width, armchair GNRs are semiconducting or metallic and zigzag GNRs are always metallic. The energy gap of GNRs scales inversely with their width. The band gap opens in armchair nanoribbon due to the quantum confinement effect and in zigzag nanoribbon the gap appears due to edge magnetization.[18-22]

Phenylalanine, a building block of protein belongs to the class of aromatic amino acids. There are three forms of phenylalanine:D-phenylalanine,L-phenylalanine and DL-phenylalanine. L-phenylalanine is an essential amino acid and is the only form of phenylalanine found in proteins. Studies based on amino acid profiling have confirmed that amino acid levels show significant differences between cancer patients and healthy donors and may serve as one of the biological markers for cancer patients.[23,24] Recently, tumor-dependent increase of serum amino acid levels in breast cancer patients have been investigated for fifteen different amino acids. It was reported that eight out of fifteen amino acid levels were significantly higher in breast cancer patients than healthy donors. Out of the eight different amino acids, L-Phenylalanine is one of the amino acid showing increased expression in the breast cancer gene viz;BRCA in the preoperative serum.[25] Moreover,amino acid rich substrate could inhibit tumor growth by initiating apoptosis in a murine model have been reported.[26] Further, reports suggest that the combined use of hyperthermia and L-phenylalanine mustard provided the greatest induction of apoptosis and therapeutic benefit.[27]

The presence of edge states[28], chemical reactivity[29], robustness[30]and tunability[31,32] nature of ZGNR makes it a promising material for future as a drug carrier in drug delivery applications. More recently, DFT studies on the physisorption of the drug paracetamol with zigzag graphene nanoribbon in terms of variation in the electrical characteristics for fabricating the biosensor devices have been reported.[33] Further, the interaction of linear polyaromatic hydrocarbons such as anthracene on ZGNR device with and without boron and nitrogen doping to check for the variation in the transport properties of the system have been investigated.[34] Experimental studies on the role of PEGylated nano graphene sheets showing interesting in vivo behaviors including highly efficient tumor passive targeting in mice model have been reprted.[35] Studies based on nanoparticle mediated hyperthermia for cancer treatment has more advantages compared to traditional methods have been reported.[36] Experimental studies based on functionalized carbon nanostructures with increasing binding affinity towards various cancer drugs by tuning their electronic properties and making the nanostructure to act as an ideal nano carrier for anticancer drugs have been formulated.[37-39]Theoretical studies using DFT on the electron transport properties through open molecular structure[47] and carbon-dimer based molecular devices[58] have been reported.Furthermore, the interaction of aromatic amino acids with graphene oxide and graphene flakes have been reported for the four amino acids via; tyrosine (Tyr), tryptophan(Trp), phenylalanine(Phe) and histidine (His).[40] Due to the strong π-π stacking, the graphene materials are poorly soluble in most of the aqueous solutions. As solubility plays a major role in drug delivery applications, few experimental and theoretical studies based on chemical functionalization of graphene nanoribbons have been developed.[41-43]

Inspired by these ideas, we performed the DFT-LSDA calculations on zigzag graphene nanoribbon (ZGNR) of width (6,0). The calculations were done by introducing antiferromagnetic spin polarized states between the edge carbon atoms of bare zigzag graphene nanoribbon (bZGNR) and the amino acid functionalized zigzag graphene nanoribbon (fZGNR).The functionalization was done by replacing one of the hydrogen atom at the edge of ZGNR using the amino side chain (-NH_2) of aromatic amino acid L-Phenylalanine. The fZGNR yielded a polar covalent bond, supported by the creation of dipole moment in the optimized structure. Thus, we find that the amino acid prefers to be functionalized at the edge of ZGNR thereby inducing a solubility change[54,55] which may be due to the partial charge transfer between the two systems.

2. Computational Methods:

The geometry optimization of the supercell[44] structures of bZGNR and fZGNR was done within the framework of first principles DFT studies using the Atomistix Tool Kit-Virtual Nano Lab (ATK-VNL) package [45,46]The C-C and C-H bond lengths in ZGNR are set to be 1.42 Å and 1.09 Å,respectively The vacuum padding along the x and y directions were set to be >10 Å in order to avoid electrostatic interaction between the repeated images in the supercell. The mesh cut off was set to be 150 Ry. Spin polarized calculations was done using the local spin density approximation (LSDA) basis set with Perdew-Zunger exchange correlation energy functional.[48] The structures were optimized until the Hellmann-Feynman force[49] on each atom was less than 0.05 eV/Å. Sampling of the Brillouin zone using the Monkhorst-Pack Scheme[50] was done with the a k-point grid of 1x1x150 for structure relaxation. The total energy convergence was done by varying the k points till

210.The optimized structures of the spin polarized ZGNR system with and without functionalization viz; bZGNR and fZGNR is shown in Fig1a* and Fig 1b*, respectively.The equilibrium geometry and the electronic properties of the two systems have been   calculated.
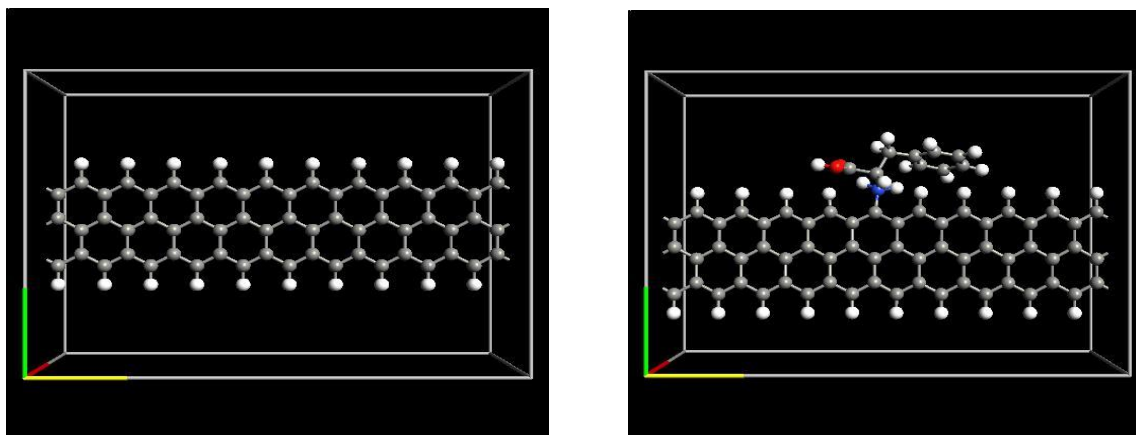

Fig1a*:Optimized structure of bZGNR (6,0)   Fig1b*:Optimized structure of fZGNR (6,0)
*Grey colour: Carbon atom, White Colour:Hydrogen atom,
Blue colour:Nitogen atom and Red colour:Oxygen atom.

3. Results and discussion:

3.1 Equlibrium Geometry:

For the bZGNR as shown in Fig 2a, the optimized C-C and C-H bond length increases from 1.42 Å and 1.09 Å to 1.46 Å and 1.159 Å,respectively. While, the C-C-H bond angle decreases from 120° to 119.66° and the C-C-C bond angle increases from 120° to 120.7°. The increase in C-C and C-H bond length of bZGNR produces a negligible variation in the bond angle which results in a minor buckling of the structure as shown in Fig 3a. For the fZGNR as shown in Fig 2b, the optimized C-C bond length increases from 1.42 Å to 1.46 Å which is same as the optimized C-C bond length of bZGNR. However, the optimized C-N bond length of fZGNR increases from 1.091 Å to 1.453 Å, thereby confirming a covalent bond formation in fZGNR. Furthermore, the C-C-N bond angles of fZGNR at the functionalization site changes to 122.02 Å ,112.85 Å and 125.18 Å, respectively.The increase of C-N bond length of fZGNR shows a partial increase and a partial decrease of bond angles ,thereby ,predicting a mixed transition state containing both sp^2 and sp^3 hybdrization similar to the results obtained for ab intio studies of carboxylated graphene[51]. Hence, due to functionalization of ZGNR, a mixed hybridization state containing both sp^2 and sp^3 character is produced which creates a significant buckling[51] in the fZGNR as shown in Fig 3b.
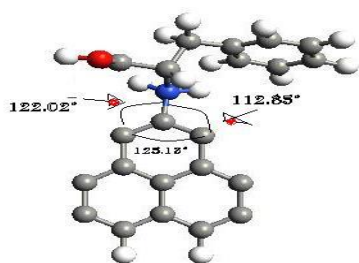

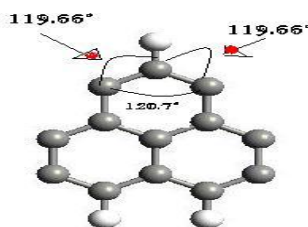**Fig 2a: Bond angles in bZGNR   Fig 2b: Bond angles in fZGNR**
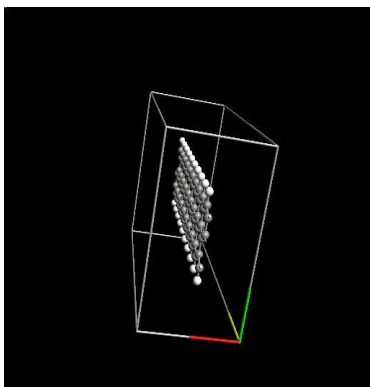
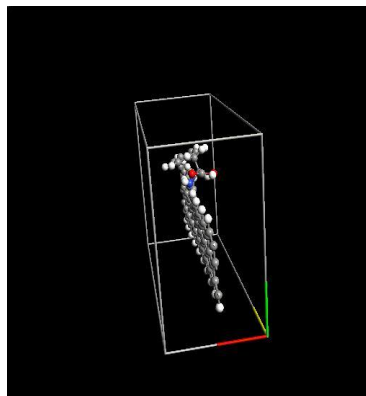**Fig 3a: Buckling in bZGNR side view**   **Fig 3b: Buckling in fZGNR side view**

The distance between the hydrogen (H) atoms of bZGNR is found to be 2.46 Å. Whereas,The distance between the amino acid functional group and the nearest H atom in fZGNR is found to be 2.76 Å (left side of L-Phenylalanine) and 2.51 Å (right side of L-Phenylalanine). Hence, functionalization of ZGNR produces structural changes in the fZGNR system,leading to the tilted nature of C-N bond length which is almost in plane with the C-C atoms of ZGNR. The results obtained are similar to the studies of selective functionalization of graphene nanoribbon (GNR) to test for the change in solubility due to the structural changes produced in GNR.[43]

3.2   Electronic Properties:

3.2 a) Total energy and electron density analysis:

The total energy of bZGNR and fZGNR is calculated to be -9717.24 eVand –12420.95 eV, respectively.The decrease in total energy for the fZGNR predicts the stability of the system which is validated by the covalent bond formation between the carbon atom of ZGNR and nitrogen atom of L-Phenylalanine, as shown in Fig 4. Moreover, within the framework of density functional theory (DFT), total energy is a functional of electron density. As shown in Table 1,the electron density of bZGNR and fZGNR decreases from 1.8821 e^{-04} $1/Å^2$ to 1.6592 e^{-04} $1/Å^2$ .Further, the reduction in total energy for fZGNR indicates a more bound system which is validated by the decrease in electron density.
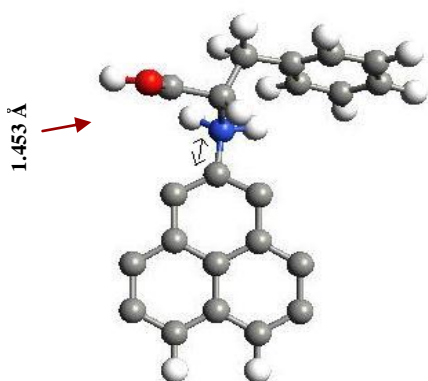

Fig 4: Covalent bond formation between the C-N atoms in fZGNR

3.2 b) *Fermi energy, dipole moment and charge transfer analysis:*

The Fermi energy of bZGNR and fZGNR is analyzed to be -5.3487 eV and -4.9291 eV, respectively. In our study, an upward shift in the Fermi level of fZGNR ocuurs due to the presence of lone pair of π electrons present in the Nitrogen(N) atom of L-Phenylalanine. As shown in Table 1,the upward Fermi shift increases the electron kinetic energy and chemical reactivity for the fZGNR system. The obtained results for the Fermi

energy are similar to the experimental studies on synthesis, properties and applications of graphene and graphene oxide[60] and DFT studies on AGNR and ZGNR with boron and nitrogen doping.[52] The dipole moment analysis have been done for the bZGNR and fZGNR systems. The results obtained are found to be similar to the interaction studies of amino acid.[53] & Charge transfer calculated for the systems bZGNR and fZGNR.The negative value indicates that charge is transferred from the amino acid L-Phenylalanine to ZGNR.

Table 1: Equilibrium geometry and electronic properties of bZGNR and fZGNR systems.

Equilibrium geometry and electronic Properties	Spin polarized system	
	ZGNR with hydrogen passivation	**ZGNR functionalized with L-Phenylalanine**
Bond Length d* (Å)	1.159	1.453
Total Energy (eV)	-9717.24	-12420.95
Kinetic Energy (eV)	6311.071	8136.414
Fermi Energy (eV)	-5.3487	-4.9291
Dipole Moment μ (D)	4.9077	9.8526
Charge Transfer$^{\&}$ (e)	ZGNR = -0.032	ZGNR= -0.604 L-Phenylalanine= +0.803
Electron Density $1/Å^2$	$1.8821 \times e^{-04}$	$1.6592 \times e^{-04}$
Band Gap (Spin Up Channel) eV	0.3557	0.1924
Band Gap (Spin Down Channel) eV	0.3557	0.2463

*C-H and C-C bond length calculated with respect to the site of functionalization for bZGNR and fZGNR.

The fZGNR system acquires a higher dipole moment of 9.8526 D in comparison to the bZGNR which has a lower dipole moment of 4.9077 D. The increase in dipole moment of the fZGNR system indicates a partial charge transfer between ZGNR and amino acid through polar covalent bond formation which is consistent with the results obtained for ab initio studies on carboxylated graphene[51] and preferential functionalization of graphene nanoribbon(GNR).[42]

The charge transfer analysis is calculated for our bZGNR and fZGNR systems using the Mulliken population studies.The charge transfer is found to be the least -0.03 e for the bZGNR system which correlates to the low value of dipole moment obtained for bZGNR. Whereas, the fZGNR system demonstrates a maximum charge transfer of -0.604 e for ZGNR and +0.803 e for L-Phenylalanine as shown in Table 1, suggesting a high favourability for functionalization at the edges of ZGNR. Our results for charge transfer in fZGNR are consistent with the DFT studies on noncovalent functionalization of pyrazinmide chemotherapeutic with graphene and its prototypes.[57]The dipole moment and charge transfer analysis for fZGNR suggest a nucleophilic behavior for ZGNR and an electrophilic behavior for the amino acid L-Phenylalanine which is consistent with DFT studies on adsorbtion of molecules on carbon nanostructures making them to act as an electron acceptor[59].

3.2 c) *Band structure analysis:*

The electronic band structures of bZGNR and fZGNR as shown in Fig 5a and Fig 5b have been investigated.The presence of antiferromagnetic coupling due to spin polarization at the opposite edge carbon atoms in bZGNR retains the spin degeneracy by opening a bandgap of 0.3557 eV between both the spin-up and spin-down channels.Whereas, for the fZGNR a band gap of 0.1924 eV for the spin-up channel and 0.2463 eV for the spin-down channel is created. The obtained results of bandgap for the fZGNR suggest the breaking of spin degeneracy and creation of spin-polarized half-semiconducting state which is similar to the results predicted for the electronic and spin properties of edge functionalized graphene nanoribbon.[56]Moreover, the lowering of band gap for both the spin channels in the fZGNR suggest the inclusion of additional energy states from the –NH$_2$ group of L-Phenylalanine into ZGNR.
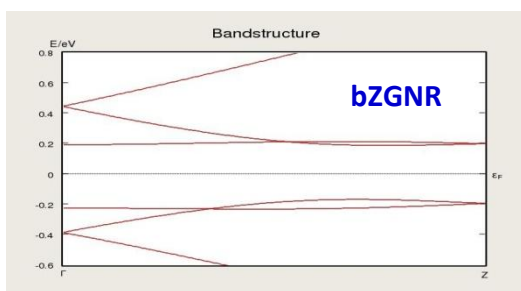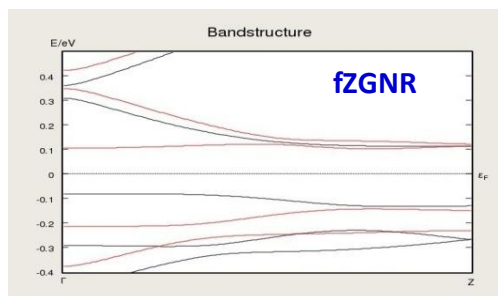
Fig 5a: Band structure of bZGNR   **Fig 5b: Band structure of fZGNR**

4. Conclusions:

We performed spin polarized DFT calculations on covalent functionalization of ZGNR with L-Phenylalanine. Our calculations suggest that amino acids could be covalently functionalized at the edge of ZGNR due to the formation of a polar covalent bond. The functionalization assisted with spin polarized calculations created significant structural modifications in the ZGNR by tuning the electronic properties without affecting its stability. Our results suggest an enhanced chemical reactivity for the functionalized system Thus, the study provides a valuable tool for understanding the nature of interaction between the amino acid and carbon nanostructures and suggest the possibility to use functionalized ZGNR for biosensing and drug delivery applications.

Acknowledgements:

References:

1. Novoselov K.S, Geim A.K, Morozov S.V, Jiang D, Zhang Y, Dubonos S.V, Grigorieva I.V and Filrsov A.A. Electric Field effect in Atomically Thin Carbon Films. Science., 2004, 306;666.
2. Young-Jun Yu, Yue Zhao, Sunmin Ryu, Louis E. Brus, Kwang S. Kim and Philip Kim. Tuning the graphene work function by electric field effect. Nano let.,2009, 9; 3430–3434.
3. Wang Z. F., Qunxiang Li, Huaixiu Zheng, Hao Ren, Haibin Su, Shi Q. W. and Jie Chen. Tuning the electronic structure of graphene nanoribbons through chemical edge modification. Phys. Rev. B., 2007, 75; 113406.
4. Changgu Lee, Xiaoding Wei,Jeffrey W. Kysar and James Hone. Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. Science., 2008,321;385-388.
5. By Haiqun Chen, Marc B. Mu¨ller, Kerry J. Gilmore, Gordon G. Wallace, and Dan Li. Mechanically Strong, Electrically Conductive, and Biocompatible Graphene Paper. Adv. Mater., 2008, 20; 3557–3561.
6. Thinnest graphene sheets react strongly with hydrogen atoms; thicker sheets are relatively unaffected. Phys.org.,2013.
7. Denis P. A and Iribarne F. Comparative Study of Defect Reactivity in Graphene J. Phys. Chem. C.,2013, 117; 19048.
8. Lee C, Wei X, Kysar J. W and Hone J. Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. Science.,2008, 321; 385–388.
9. Bolotin K.I., Sikes K.J., Jiang Z., Klima M., Fudenberg G., Hone J., Kim.P and Stormer H. L., Solid State Commun., 2008 ,146 ;351.
10. Morozov S.V., Novoselov K. S., Katsnelson M.I., Schedin F.,. Elias D. C, Jaszczak J.A and Geim A. K. Giant Intrinsic Carrier Mobilities in Graphene and Its Bilayer. Phys. Rev. Lett., 2008, 100; 016602.
11. Deivasigamani Umadevi and Narahari Sastry .G. Quantum Mechanical Study of Physisorption of Nucleobases on Carbon Materials: Graphene versus Carbon Nanotubes. J. Phys. Chem. Lett., 2011, 2 ; 1572.
12. Panchokarla L.S, Subrahmanyam K. S, Saha S. K, Govindaraj A, Krishnamurthy H. R, Waghmare U. V and C. N. R. Rao. Synthesis, Structure, and Properties of Boron- and Nitrogen-Doped Graphene, Adv. Mater., 2009, 21; 4726.

13. Lherbier.A,Blase.X,Niquet.YM,Triozon. F and Roche.S. Charge Transport in Chemically Doped 2D Graphene. Phys. Rev. Lett., 2008, 101; 036808.

14. Loh K.P.,Bao .Q, Ang.PK, Yang JX. The Chemistry of Graphene. J. Mater.Chem.,2010, 20; 2277.

15. Cracium M.F, Khrapach I, Barnes M.D. and Russo S. Properties and applications of chemically functionalized graphene. J. Phys. Condens. Matter.,2013, 25; 423201.

16. Fujita M, Wakabayashi K, Nakada K and Kusakabe K. Peculiar Localized State at Zigzag Graphite Edge .J. Phys. Soc. Jpn., 1996, 65; 1920-1923.

17. Nakada K, Fujita M, Dresselhaus G and Dresselhaus M.S. Edge state in graphene ribbons: Nanometer size effect and edge shape dependence. Phys. Rev. B .,1996, 54; 17954-17961.

18. Barone V, Hod O, and Scuseria G. E. Electronic Structure and Stability of Semiconducting Graphene Nanoribbons. Nano Lett.,2006, 6; 2748–2754.

19. Melinda Y. Han, Barbaros Özyilmaz, Yuanbo Zhang and Philip Kim. Energy Band-Gap Engineering of Graphene Nanoribbons. Phys. Rev. Lett., 2007,98; 206805.

20. Levente Tapasztó, Gergely Dobrik, Philippe Lambin and László P. Biró. Tailoring the atomic structure of graphene nanoribbons by scanning tunnelling microscope lithography. Nature Nanotechnology .,2008, 3; 397 – 401.

21. Young-Woo Son, Marvin L. Cohen and Steven G. Louie. Energy Gaps in Graphene Nanoribbons. Phys. Rev. Lett., 2006,97;216803.

22. Jung .J, Pereg-Barnea .T and MacDonald A. H. Theory of Interedge Superexchange in Zigzag Edge Magnetism. Phys. Rev. Lett., 2009,102; 227205.

23. Lai HS, Lee JC, Lee PH, Wang ST and Chen WJ. Plasma free amino acid profilein cancer patients. Semin Cancer Biol., 2005, 15;267–276.

24. Miyagi Y, Higashiyama M, Gochi A, Akaike M, Ishikawa T, Miura T, Saruki N,Bando E, Kimura H, Imamura F, Moriyama M, Ikeda I, Chiba A, Oshita F,Imaizumi A, Yamamoto H, Miyano H, Horimoto K, Tochikubo O, Mitsushima T, Yamakado M and Okamoto N. Plasma free amino Acid profiling of fivetypes of cancer patients and its application for early detection. PLoS One .,2011, 6;e24143.

25. Isabel Poschke, Yumeng Mao, Rolf Kiessling and Jan de Boniface. Tumor-dependent increase of serum amino acid levels in breast cancer patients has diagnostic potential and correlates with molecular tumor subtypes. Journal of Translational Medicine., 2013,11;290.

26. Kulcsar G, Gaal D, Kulcsar PI, Schulcz A and Czompoly T. A mixture of aminoacids and other small molecules present in the serum suppresses thegrowth of murine and human tumors in vivo. Int J Cancer.,2013, 132; 1213–1221.

27. Omar I Abdel-Wahab, Elizabeth Grubbs, Benjamin L Viglianti, Tsung-Yen Cheng,Tomio Ueno, SaeHee Ko, Zahid Rabbani, Simon Curtis, Scott K. Pruitt, Mark W. Dewhirst and Doug S. Tyler. The Role of Hyperthermia in Regional Alkylating Agent Chemotherapy. Clin Cancer Res.,2004, 10; 5919-5929.

28. Katsunori Wakabayashi, Yositake Takane, Masayuki Yamamoto and Manfred Sigrist. Electronic transport properties of graphene nanoribbons. New J. Phys., 2009, 11; 095016.

29. De-en Jiang, Bobby G. Sumpter and Sheng Dai. The unique chemical reactivity of a graphene nanoribbon's zigzag edge. J. Chem. Phys.,2007, 126; 134701.

30. Nima Djavid, Kaveh Khaliji, Seyed Mohammad Tabatabaei, and Mahdi Pourfath. A Computational Study on the Electronic TransportProperties of Ultranarrow Disordered ZigzagGraphene Nanoribbons. IEEE Transactions on Electron Devices.,2014,61;23-29.

31. Li Yang, Cheol-Hwan Park, Young-Woo Son, Marvin L. Cohen and Steven G. Louie. Quasiparticle Energies and Band Gaps in Graphene Nanoribbons. Phys. Rev. Lett.,2007, 99; 186801.

32. Hosik Lee, Young-Woo Son, Noejung Park, Seungwu Han and Jaejun Yu. Magnetic ordering at the edges of graphitic fragments: Magnetic tail interactions between the edge-localized states. Phys. Rev. B., 2005, 72; 174431.

33. Janani K, Preferencial Kala C, Hariharan RM, Sivasathya S and John Thiruvadigal D. Electron Transport of Zigzag Graphene Nanoribbon Based Biosensor-A Future Perspective towards Biosensor and Biomedical Applications. Austin J Nanomed Nanotechnol .,2014.2; 1-5.

34. R. Chowdhury,Adhikari.S, Rees.P and Wilks S.P. Graphene-based biosensor using transport properties. Phys. Rev. B.,2011,83; 045401.

35. KaiYang, Shuai Zhang, Guoxin Zhang, Xiaoming Sun, Shuit-Tong Lee and Zhuang Liu. Graphene in Mice: Ultrahigh In Vivo Tumor Uptake and Efficient Photothermal Therapy. Nano Lett.,2010, 10;3318–3323.

36. Dev Kumar Chatterjee,Parmeswaran Diagaradjane and Sunil Krishnan. Nanoparticle-mediated hyperthermia in cancer therapy. Ther Deliv., 2011, 2; 1001–1014. [PubMed: 22506095].

37.   Mauro Ferrari. Cancer Nanotechnology: Opportunities and Challenges.Nature Reviews Cancer.,2005, 5; 161-171. [PubMed: 15738981].

38.   Thakare VS, Das M, Jain AK, Patil S and Jain S. Carbon nanotubes in cancer theragnosis. Nanomedicine (Lond)., 2010, 5;1277-1301. [PubMed: 21039202].

39.   Zhang W1, Zhang Z andZhang Y. The application of carbon nanotubes in target drug delivery systems for cancer therapies. Nanoscale Res Lett., 2011, 6; 555. [PubMed: 21995320].

40.   HakkimVovusha, SuparnaSanyal, and BiplabSanyal. Interaction of Nucleobases and Aromatic Amino Acids with Graphene Oxide and Graphene Flakes. J. Phys. Chem. Lett.,2013, 4; 3710–3718.

41.   Bostjan Genorio and Andrej Znidarsic. Functionalization of graphene nanoribbons. J. Phys. D: Appl. Phys.,2014, 47; 094012.

42.   Hoonkyung Lee. Preferential functionalization on zigzag graphene nanoribbons: first-principles calculations. J. Phys.: Condens. Matter. 2010, 22; 352205.

43.   Hoonkyung Lee, Marvin L. Cohen and Steven G. Louie. Selective functionalization of halogens on zigzag graphene nanoribbons: A route to the separation of zigzag graphene nanoribbons. Appl. Phys. Lett.,2010, 97; 233101.

44.   Marvin L. Cohen,Schlüter.M, James.R,Chelikowsky and Steven G. Louie. Self-consistent pseudopotential method for localized configurations: Molecules.Phys.Rev.B.,1975,12; 5575.

45.   Atomistix Tool Kit Version 12.8.2. www.quantumwise.com

46.   Soler J.M, Artacho E, Gale J.D, Garcı´a A, Junquera J, Ordejo´n P and Sa´nchez-Portal D. The SIESTA method for ab initio order-N materials simulation. J. Phys. Condens. Matter.,2002, 14; 2745.

47.   Preferencial Kala C, Aruna Priya P and John Thiruvadigal D. Investigation of terminal group effect of electron transport through open molecular structure. Communication in Theoretical Physics.,2013, 59: 649-654.

48.   Perdew J.P. and Alex Zunger. Self-interaction correction to density-functional approximations for many-electron systems. Phys. Rev. B.,1981, 23; 5048-79.

49.   H. Hellmann. Einführung in die Quantenchemie. Leipzig: Franz Deuticke. 1937, Sec. 54; R.P. Feynmann. Forces in Molecules. Phys. Rev.,1939, 56, 340-343.

50.   HJ Monkhorst and JD Pack. Special points for Brillouin-zone integrations. Phys. Rev. B.,1976, 13; 5188-5192.

51.   Nabil Al-Aqtash and Igor Vasiliev. Ab Initio Study of Carboxylated Graphene.J. Phys. Chem. C., 2009, 113 ;12970.

52.   Satyendra Singh Chauhan,Pankaj Srivastava and Ashwani Kumar Shrivastava. Electronic and transport properties of boron and nitrogen doped graphene nanoribbons: an ab initio approach. Appl. Nanosci., 2014, 4; 461.

53.   Chinagandham Rajesh, Chiranjib Majumder, Hiroshi Mizuseki and Yoshiyuki Kawazoe. A theoretical study on the interaction of aromatic amino acids with graphene and single walled carbon nanotube. The Journal of Chemical Physics.,2009, 130; 124911.

54.   Sharma R, Baik JH, Perera CJ and Strano MS. Anomalously large reactivity of single graphene layers and edges toward electron transfer chemistries. Nano Lett., 2010, 10; 398-405.[PubMed : 20055430].

55.   Zhengzong Sun, Shin-ichiro Kohama, Zengxing Zhang, Jay R. Lomeda and James M. Tour. Soluble Graphene Through Edge-Selective Functionalization. Nano Res.,2010, 3;117–125.

56.   Cervantes-Sodi.F, Csányi.G, Pisane.S and FerrariA.C. Edge-funtionalized and substitutional doped graphene nanoribbons: electronic and spin properties. Phys. Rev. B.,2008,77; 165427.

57.   Nabanita Saikia and Ramesh C. Deka. Density functional study on noncovalent functionalization of pyrazinamide chemotherapeutic with graphene and its prototypes. New J. Chem., 2014,38; 1116-1128.

58.   Hariharan R.M and Thiruvadigal D.J.Effect of different metallic electrodes on transport properties of a carbon-dimer based molecular devices. Asian Journal of Chemistry.,2013,Volume 25; S445-S448.

59.   Sivasathya.S,JohnThiruvadigal.D and MathiJaya.S. Electron transport through metallic single wall carbon nanotubes with adsorbed NO_2 and NH_3 molecules:A first-principles study. Chemical Physics Letters.,2014,609;76-81.

60.   Yanwu Zhu,Shanthi Murali,Weiwei Cai,Xuesong Li, Ji Won Suk, Jeffrey R. Potts and Rodney S. Ruoff . Graphene and Graphene Oxide: Synthesis, Properties and Applications. Adv. Mater.,2010, XX; 1–19.

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