Research Article | DOI:10.5281/zenodo.10403167
www.jnanosam.com

NANOSAM
Journal of NanoScience in Advanced Materials

Impacts of Fe and Ru Atomic Dopants on the Structural and Electronic Features of a Graphene Flake: DFT Outlook

Muhammad Da'i[1], Osman Murat Ozkendir[2], and Mahmoud Mirzaei[2#]

Density functional theory (DFT) calculations were performed for investigating the impacts of iron (Fe) and ruthenium (Ru) on the structural and electronic features of a graphene (Gr) flake for providing insights into the customization of nanostructures for desired purposes. The results indicated a planar stability for each of FeGr and RuGr models, in which the central area of both models were wider than the pure Gr model. Additionally, the electronic molecular orbital features indicated the variations of frontier molecular orbital levels in the atomic doped models but with different changes for the FeGr and RuGr models in comparison with the pure Gr model. While the FeGr model was proposed to work as a better conductor in comparison with the pure Gr, the RuGr model was proposed to work as a batter capacitor. Variation of molecular orbitals of both models were significant to be monitored by the diagrams of density of states (DOS) and their quantitative values indicated characteristic and unique features for the doped models. Finally, the features of FeGr and RuGr customized them for the specific applications of better conductors of better capacitors.

1. Introduction

Exploring novel materials and related processes are among the most important topics of science and engineering issues [1,2]. Especially after the innovation of nanostructures, further analyses showed the importance of composition of these novel materials for assigning their future functions and applications [3,4]. In this regard, both of generating newly composed nanostructures or implementing atomic dopants in the carbon nanostructures have been found applicable for approaching the purpose [5,6]. The hetero-composed materials have advantages of customization for approaching the specific applications [7,8]. To this aim, metal-atomic doped nanostructures have been seen even more useful regarding their characteristic features especially for managing the electronic behavior of the new doped models [9,10]. Among the metal atoms, heavy ones were found important to provide more electronic orbitals for the doped nanostructure for preparing them for contributing to further interactions and reactions [11,12]. Based on the various types of nanostructures, the planar graphene with a high surface area has been found very suitable for working as an adsorbent to approach a sensor/detector function [13,14]. The pure carbon surface of graphene is a unique electronic surface, ~~in which its~~ modification and decoration by atomic dopants could bring new features for the decorated graphene even better than the original one [15,16]. To this point, the current work was done to recognize the impacts of iron (Fe) and ruthenium (Ru) atomic dopants on the structural and electronic features of a graphene (Gr) flake along with density functional theory (DFT) calculations.

As shown in Figure 1, the molecular models were represented in the pure (Gr) and doped (FeGr and RuGr) forms to show the decoration of original graphene flake for approaching the purpose of this work. All the models were optimized and their stabilized structures were obtained to be assessed for performing the required electronic analyses. Exploring the molecular models has an advantage of investigating the small-scale systems, in which learning their details along with molecular computations could reveal insights into the original states excluding all unwanted interferers [17,18]. Additionally, the results of earlier works indicated the role of molecular investigations for developing further applications of nanostructures [19,20]. Accordingly, exploring the structural and electronic variations of Gr, FeGr, and RuGr models were done

[1] *Faculty of Pharmacy, Universitas Muhammadiyah Surakarta, Surakarta, Indonesia,* [2] *Laboratory of Molecular Computations (LMC), Department of Natural and Mathematical Sciences, Faculty of Engineering, Tarsus University, Tarsus, Türkiye*
[#]*Corresponding author:* mahmoudmirzaei@tarsus.edu.tr (M. Mirzaei)

Keywords: Atomic Dopant; Density Functional Theory; Electronic Structure; Graphene.

Received: 30 September 2023 | Accepted: 29 October 2023 | Published: 22 December 2023

NANOSAM
Journal of NanoScience in Advanced Materials

in the current work to assess their characteristic features for further applications in sensor/detector related devices. The models were compared in the pure and doped states to show the impacts of atomic dopants. In this regard, the characteristic atomic and molecular features of the investigated systems were evaluated in both of quantitative and qualitative terms to be carefully discussed for approaching the goal of this work to introduce a novel doped graphene system.

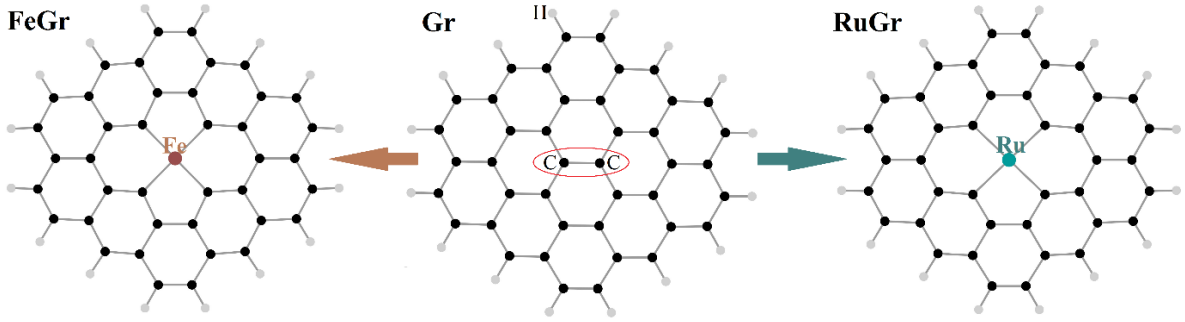

Figure 1. The optimized molecular models of Gr, FeGr, and RuGr; the dopant area of Gr was shown in red.

2. Results and Discussion

The main goal of this work was the investigation of impacts of Fe and Ru atomic dopants on the structural and electronic features of a graphene flake, in which the required data were obtained by performing DFT calculations. As shown in Figure 1, three models were investigated in this work including the pure graphene (Gr) and each of Fe and Ru doped (FeGr and RuGr) models. To make the doped models, two carbon atoms of Gr were replaced by one of Fe or Ru atoms to produce the FeGr and RuGr models, in which the new bond lengths were optimized for the structure as 1.89 Å for C-Fe and 2.01 Å for C-Ru in contrast with the earlier 1.41 Å for C-C. The original Gr model was a planar model and the doped models were also remained in a planar state not to change the characteristic feature of graphene monolayer. The additional hydrogen atoms were indeed the terminating atoms of graphene flake to mimic the sp^2 hybridization for the carbon atoms at the edge of investigated flake excluding any dangling effects for the structure [21]. In this case, the electrons of all atoms were paired and the molecular system was located in a singlet ground state representing a stabilized structure. It was found that the effects of atomic dopants were almost locally significant for the atomic positions of other carbon atoms of the flake to keep the existence of a small concentration of atomic dopants in the original structure. As a result, two planar atomic doped models were found with a similarity of planar state to the pure graphene flake. However, providing a longer C-Fe and C-Ru distances inside the flake could lead to provide a more vacancy for trapping other substances especially in the case of interactions and reactions with other substances. Hence, the surface could be expected more suitable for the purpose.

Based on the results of earlier works on the application of graphene nanostructure for adsorbing other substances, the existence of a vacancy or doped region was an advantage of decorated surface for involving in more efficient reactions and interactions with other substances [22]. The achievement of structural features of optimized FeGr and RuGr models indicated the customization of models for providing a wider central region for the doped region of RuGr model in comparison with the doped region of FeGr model. However, the surrounding atoms of metal-dopant was under more pressure or rearrangement in the RuGr model in comparison with the same atomic regions of FeGr model. Although the pressure of rearranging the surrounding atom was significant, but the effect on the geometers of second neighboring atoms was almost negligible and the planar model was stabilized. Hence, based on the required features of further applications, the models could be categorized to work in a customized region of FeGr or RuGr. Both of Fe and Ru are in the same group (Group 8B) of transition metals of elements table but in different rows as Fe was located in the 4th row and Ru was located in the 5th row. Accordingly, the longer atomic radius of Ru than that of Fe leaded to a longer distance of C-Ru bond than that of C-Fe bond. It could be mentioned that because of requiring different structural conformations for working in different purposes, the models could be customized upon the addition of a low concentration of dopant and the obtained structure could be known as a doped system. In the case of current work, the stoichiometry of Gr was changed from $C_{42}H_{16}$ to $FeC_{40}H_{16}$ and $RuC_{40}H_{16}$ in the doped models in a low concentration of dopant existence. A wider central area was obtained for the doped models by implementing such a low concentration of Fe and Ru atomic dopants in them.

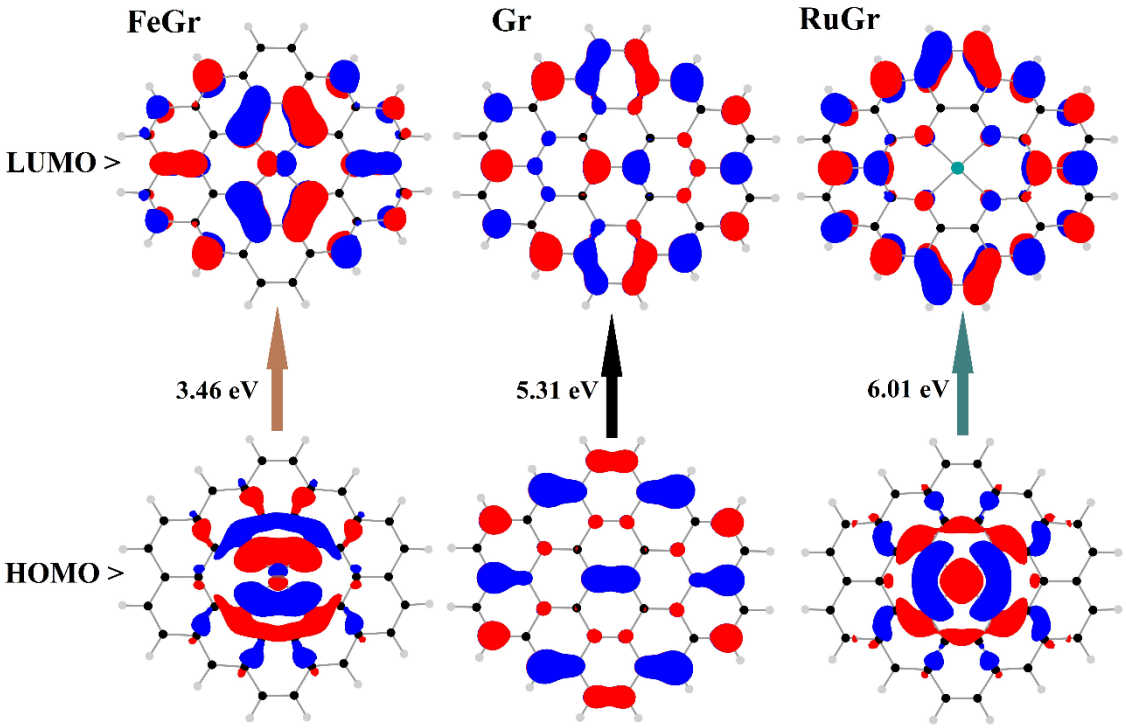

Figure 2. The HOMO-LUMO distribution patterns of optimized molecular models of Gr, FeGr, and RuGr; the energy gap (E_{gap}) distances were written besides the vertical arrows.

As a conclusion, an advantage of implemented atomic dopants could be found for providing wider central areas of FeGr and RuGr flakes.

The electronic molecular orbital features of the optimized models were analyzed based on the exact energy values of the main frontier molecular levels; HOMO and LUMO. The highest occupied molecular orbital is assigned by HOMO and the lowest unoccupied molecular orbital is assigned by LUMO. It should be mentioned that the current work was done based on performing molecular computations and the periodic boundary conditions were not employed within the calculations. The structures were single-standing models, and they were stabilized by optimization calculations prior to evaluating their electronic features. In Figure 2, the HOMO and LUMO distribution patterns were shown for Gr, FeGr, and RuGr molecular models. At a first look, it could be recognized that the models were significantly distinguished from each other regarding the distribution patterns of dominant HOMO and LUMO levels. Hence, different electronic properties could be expected for the doped models in comparison with the Gr model. Further quantitative results were tabulated in Table 1. As described by the exact values of energies for HOMO and LUMO and also the energy gap (E_{gap}) distance, the FeGr model detected a more conductivity feature than the pure Gr model whereas the RuGr model detected a more isolation feature than the pure Gr model. Although both of Fe and Ru metal atoms were at the same group of elements table, their impacts were completely different for the investigated graphene flake even in an opposite direction. To this point, the results indicated an importance of customization of nanostructures for approaching desired purposes as indicated by a more conductivity of FeGr and a more isolation of RuGr regarding the referenced Gr model.

The obtained quantities of electronic molecular orbital features of optimized molecular models of Gr, FeGr, and RuGr were summarized in Table 1 including the exact energies of HOMO and LUMO levels, energy gap (E_{gap}), chemical hardness and chemical potential. The exact energy values of HOMO and LUMO were calculated directly, and the values of E_{gap} were obtained by the difference of HOMO and LUMO levels. The chemical hardness was

Table 1. The electronic molecular orbital features of optimized molecular models of Gr, FeGr, and RuGr.

Molecular Model	HOMO eV	LUMO eV	Energy Gap eV	Hardness eV	Potential eV
FeGr	-6.69	-3.23	3.46	1.73	-4.95
GR	-6.42	-1.11	5.31	2.65	-3.76
RuGr	-6.60	-0.59	6.01	3.01	-3.59

NANOSAM
Journal of NanoScience in Advanced Materials

obtained by an average value of E_{gap} and the chemical potential was obtained by an average value of HOMO and LUMO summation. By analyzing the obtained electronic values, it was found that the HOMO and LUMO levels detected the impacts of atomic dopants in FeGr and RuGr models in comparison with the pure Gr model. However, the impact was not the same for the two doped models, in which the HOMO levels of FeGr and RuGr were moved to a lower level than the pure Gr whereas the LUMO level of FeGr significantly moved to a lower level but and that of RuGr model was moved to an upper level than the LUMO level of pure Gr. In this regard, different electronic features were evaluated for the models as was described earlier for the energy gap distance. Additionally, chemical hardness of FeGr was reduced but that of RuGr was increased meaning an easier participation of FeGr in other reactions and interactions. The values of chemical potential also affirmed such results. The diagrams of density of states (DOS) were shown in Figure 3 for illustrating the variations of molecular orbitals before and after the occupied and unoccupied frontier molecule orbital levels. In this case, the variations could show a significant change of electronic features of the FeGr than the RuGr both in comparison with the pure Gr model. As the conductance rate is proportional to an inverted value of E_{gap}, then a higher rate could be expected for the FeGr model in comparison with a lower rate for the RuGr model. As a consequence, based on the required features of models, each of Gr, FeGr, and RuGr could be employed, in which the doped models showed a general priority of employing in comparison with the pure Gr model. To emphasize on further applications of such doped systems, employing them in electronic related functions and applications are suitable. In the other words, their sensitivity and measurability of variations could be found suitable for adsorbent or sensor related functions and applications in the new customized doped models.

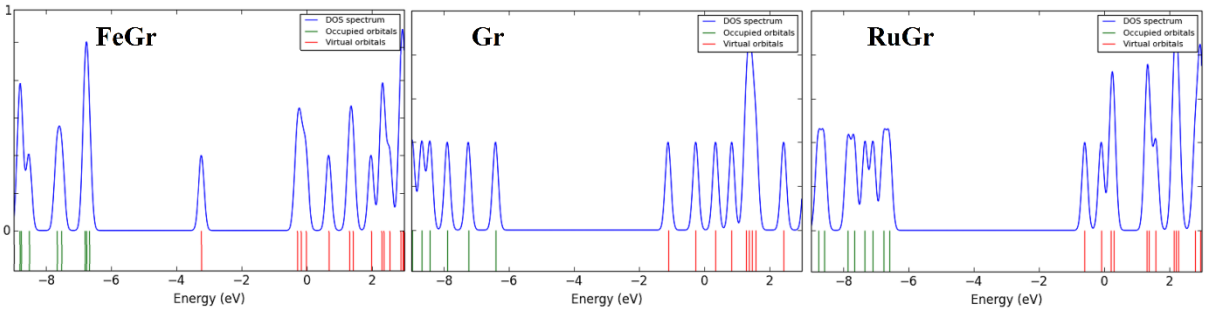

Figure 3. The DOS diagrams of optimized molecular models of Gr, FeGr, and RuGr.

3. Conclusion

The current work was done to explore impacts of Fe and Ru atomic dopants on the structural and electronic features of a graphene flake along with DFT calculations. The molecular models of Gr, FeGr, and RuGr were optimized and their stabilized structures were found. In comparison with the pure Gr, wider central areas for each of FeGr and RuGr models with the highest area for RuGr model were obtained. Additionally, the atomic doped models were also in planar states similar to the pure Gr. The obtained electronic features indicated he impacts of atomic dopants on both of HOMO and LUMO levels of doped models, but in different direction comparing to each other. The E_{gap} of FeGr was decreased and that of RuGr was increased in comparison with the referenced pure Gr flake. As a consequence, different features of conductivity were observed for the investigated models. Based on the values of chemical hardness and chemical potential, the FeGr model was that one with the highest suitability of participation in other reactions and interactions whereas the RuGr was indeed a better capacitor in this case. Based on the distribution patterns and monitoring the DOS diagrams, the models were recognizable by the variations of electronic molecular orbital features, in which the highest conductance rate and corresponding sensitivity could be expected for the FeGr model. As a consequence, customizing the nanostructures is essential for approaching a desired function and application.

Method

The molecular computations of this work were done using the Gaussian program [23] and the employed DFT level was included wB97XD functional and 3-21G* basis set, in which the LANL08 effective core potential basis set [24] was used for Fe and Ru atoms. The models were optimized to obtain their stabilized geometries (Figure 1). Next, the electronic molecular orbital features were evaluated as shown in Figures 2 and 3 and the quantities were tabulated in Table 1.

Based on performing such molecular computations, the models of this work including the pure Gr and the doped FeGr and RuGr were discussed in details.

Authors' contributions:

M.D., O.M.O., and M.M. had equivalent contributions to this manuscript; conceptualization, investigation, methodology, writing the original draft, reviewing, and editing the final version, with an additional supervision contribution for M.M.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

[1] Shi, S., Si, Y., Han, Y., Wu, T., Iqbal, M.I., Fei, B., Li, R.K., Hu, J., Qu, J., *Recent progress in protective membranes fabricated via electrospinning: Advanced materials, biomimetic structures, and functional applications,* Advanced Materials **34** (17), 2107938 (2022).

[2] Xu, H., Yan, Q., Yao, W., Lee, C.S., Tang, Y., *Mainstream optimization strategies for cathode materials of sodium-ion batteries,* Small Structures **3**(4), 2100217 (2022).

[3] Barra, A., Nunes, C., Ruiz-Hitzky, E. and Ferreira, P., *Green carbon nanostructures for functional composite materials,* International Journal of Molecular Sciences **23** (3), 1848 (2022).

[4] Kumar, N., Chamoli, P., Misra, M., Manoj, M.K. and Sharma, A., *Advanced metal and carbon nanostructures for medical, drug delivery and bio-imaging applications,* Nanoscale **14** (11), 3987 (2022).

[5] Antunes, J.M., Pereira, A.F. and Sakharova, N.A., *Overview on the evaluation of the elastic properties of non-carbon nanotubes by theoretical approaches,* Materials **15** (9), 3325 (2022).

[6] Esfahani, S., Akbari, J., Soleimani-Amiri, S., Mirzaei, M. and Ghasemi Gol, A., *Assessing the drug delivery of ibuprofen by the assistance of metal-doped graphenes: insights from density functional theory,* Diamond and Related Materials **135**, 109893 (2023).

[7] Liu, Z., He, T., Jiang, Q., Wang, W., Tang, J., *A review of heteroatomic doped two-dimensional materials as electrocatalysts for hydrogen evolution reaction,* International Journal of Hydrogen Energy **47** (69), 29698 (2022).

[8] Zhan, F., Liu, S., He, Q., Zhao, X., Wang, H., Han, M., Yamauchi, Y., Chen, L., *Metal–organic framework-derived heteroatom-doped nanoarchitectures for electrochemical energy storage: recent advances and future perspectives,* Energy Storage Materials **52**, 685 (2022).

[9] Tang, F., Xia, W., Zhang, H., Zheng, L., Zhao, Y., Ge, J. and Tang, J., *Synthesis of Fe-doped carbon hybrid composed of CNT/flake-like carbon for catalyzing oxygen reduction,* Nano Research **15** (7), 6670 (2022).

[10] Yan, Y., Yang, Q., Shang, Q., Ai, J., Yang, X., Wang, D. and Liao, G., *Ru doped graphitic carbon nitride mediated peroxymonosulfate activation for diclofenac degradation via singlet oxygen,* Chemical Engineering Journal **430**, 133174 (2022).

[11] Ci, Q., Wang, Y., Wu, B., Coy, E., Li, J.J., Jiang, D., Zhang, P. and Wang, G., *Fe-doped carbon dots as NIR-II fluorescence probe for in vivo gastric imaging and pH detection,* Advanced Science **10** (7), 2206271 (2023).

[12] He, R., Yang, P., Huang, Q. and Yang, L., *Electrospun nano-Ru doped carbon nanofibers for efficient alkaline hydrogen evolution reaction,* Chemical Physics Letters **809**, 140147 (2022).

[13] Zhang, F., Yang, K., Liu, G., Chen, Y., Wang, M., Li, S. and Li, R., *Recent advances on graphene: synthesis, properties and applications,* Composites Part A: Applied Science and Manufacturing **160**, 107051 (2022).

[14] Razaq, A., Bibi, F., Zheng, X., Papadakis, R., Jafri, S.H.M. and Li, H., *Review on graphene-, graphene oxide-, reduced graphene oxide-based flexible composites: from fabrication to applications,* Materials **15** (3), 1012 (2022).

[15] Mirzaei, M., Rasouli, A.H. and Saedi, A., *HOMO-LUMO photosensitization analyses of coronene-cytosine complexes,* Main Group Chemistry **20** (4), 565 (2021).

[16] Harismah, K., Mirzaei, M. and Moradi, R., *DFT studies of single lithium adsorption on coronene,* Zeitschrift für Naturforschung A **73** (8), 685 (2018).

[17] Sumiya, Y., Harabuchi, Y., Nagata, Y. and Maeda, S., *Quantum chemical calculations to trace back reaction paths for the prediction of reactants,* JACS Au **2** (5), 1181 (2022).

[18] Mirzaei, M., *Density functional study of defects in boron nitride nanotubes,* Zeitschrift für Physikalische Chemie **223** (7), 815 (2009).

[19] Selvam, P., Tsuboi, H., Koyama, M., Endou, A., Takaba, H., Kubo, M., Del Carpio, C.A. and Miyamoto, A., *Computational chemistry for industrial innovation,* Reviews in Chemical Engineering **22** (6), 377 (2006).

[20] Li, G. and Tan, Y., *The construction and application of asphalt molecular model based on the quantum chemistry calculation,* Fuel **308**, 122037 (2022).

[21] Yaraghi, A., Ozkendir, O.M. and Mirzaei, M., *DFT studies of 5-fluorouracil tautomers on a silicon graphene nanosheet,* Superlattices and Microstructures **85**, 784 (2015).

[22] Chen, J., Min, F., Liu, L. and Cai, C., *Systematic exploration of the interactions between Fe-doped kaolinite and coal based on DFT calculations,* Fuel **266**, 117082 (2020).

[23] Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., et al., *Gaussian 09 program,* Gaussian Inc., Wallingford, CT (2009).

[24] Pritchard, B.P., Altarawy, D., Didier, B., Gibson, T.D. and Windus, T.L., *New basis set exchange: an open, up-to-date resource for the molecular sciences community,* Journal of Chemical Information and Modeling **59** (11), 4814 (2019).