Egypt. J. Chem. **Vol. 64,** No. 1 pp. 407 - 412 (2021)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Computational Study on the Electronic Properties of Graphene/Calcium Oxide Nanocomposite

Amal H. Al-Bagawi[a] , Eid E. Salama[b,c]

[a] *Chemistry Department, Faculty of Science, University of Ha'il, 1560, Hail, KSA*
[b] *Chemistry Department, college of Science and Arts , Jouf University, Qurayyat , Kingdom of Saudi Arabia*
[c] *Chemistry Department, Faculty of Science , Suez Canal University ,Ismailia , Egypt*

Abstract

Semiempirical PM6 quantum mechanical method was used to investigate the changes in the electronic and physical parameters of graphene before and after interaction with calcium oxide (CaO). Calculations were conducted the optimized structures with graphene interacting with two CaO molecules forming G/CaO nanocomposite once through the O atom then through the Ca atom, in the form of adsorb and complex states. Results indicated the deformation of graphene structure upon interaction with CaO but the resulting G/CaO is more thermally stable than graphene itself. The studied G/CaO composites were also found to be more reactive than graphene in regard to their higher calculated total dipole moments. The calculated thermal parameters further confirmed the thermal stability of G/CaO composites.

Keywords: Graphene; CaO; Electronic properties; thermal properties; PM6.

1. Introduction

Carbon-based materials are widely used in many applications owing to their low cost, high surface area-to-volume ratio, high electrical conductivity, and high thermal stability [1-2]. They could be used in charge storage electrodes by means of physical adsorption, which renders high power density and long cycle life rather than battery-grade materials [3]. Functionalized carbon-based materials could be achieved with the help of metal oxides. Since the discovery of graphene by Novoselov et al. (2004), it became a hot topic of research owing to its unique properties [4]. Graphene is simply described as a type of new material consisting of carbon atoms with sp^2 hybridization and a flat lattice configuration with distances of approximately 0.142 nm between the carbon atoms as described earlier [5-6]. G as a nanomaterial has a high surface area and a zero band-gap energy, allowing it to act as sensor. Its unique properties such as a specific surface area of 2.6 x 103 m^2/g, high-speed electron mobility of 2.0 x 105 cm^2/Vs at room temperature, and heat conductivity of 5300 W/mK, enhance its ability to act as chemical sensor [7-9]. It was reported that metal oxide is a suitable material for improving the sensing properties of G [10]. The presence of a metal oxide together with graphene in the form of a nanocomposite to be applied as electrochemical sensors or biosensors has been reported [11-13]. The presence of metal oxides with graphene also has some advantages, such as causing structural changes that provide improvements in the

*Corresponding author e-mail: amalelbagawi@gmail.com (Amal H. Al-Bagawi).
Receive Date: 28 July 2020, Revise Date: 26 August 2020, Accept Date: 30 August 2020
DOI: 10.21608/EJCHEM.2020.37523.2771

lattice symmetry and cell parameters, and facilitating the construction of a 3D conductive porous network for improving the charge transfer pathway and electrical properties. Finally, metal oxides could induce changes in the surface properties that influence the chemical activity and conductivity of materials [13-14]. Another important application for graphene/metal oxides is also reported as storage materials, since they are considered as redox-active and have been utilized as efficient energy-storage electrodes [15-16]. Earth alkali metal oxides such as CaO have high abundance, low cost and high solubility in acids, allowing it as a catalyst material to be separated relatively easily from the carbon product [17]. The effects of chemical composition and physico-chemical properties of graphene grown over earth alkali metal oxides were studied [18]. In this regard, molecular modeling is a very useful tool that helps in effectively monitoring the changes in graphene under the influence of metal oxide. Molecular modeling provides physical, chemical and biological data for systems and molecules in different conditions covering all molecular sciences [19-22]. For graphene quantum dots, molecular modeling was used to investigate the electronic properties, structural parameters, HOMO/LUMO orbitals and Density of states DOS [24-26]. For other carbon nanomaterials, molecular modeling can also investigate surface properties through studying and mapping the molecular electrostatic potential. Such computational methods can explore the electronic properties of graphene composites in order to functionalize its applications, and to assess their potential electronic, biological and environmental applications as reported previously [27-28]. PM6 is a class of semiempirical models that gives appropriate computational accuracy within appropriate computation time. This paves the way toward the application of such models for graphene enhanced with metal oxide to follow up the changes in the charge and subsequently the total dipole moment (TDM). Several studies have already cited the various applications as well as the experimental characterization of graphene nanocomposites such as the medical application of graphene/hydroxyapatite nanocomposites [29], production of graphene oxide-based calcium carbonate/chitosan nanocomposites [30], and the different methods of preparation of graphene and its derivatives, and the production of different graphene-based inorganic nanocomposites used in numerous applications like biosensors, and electrochemical and gas sensors, supercapacitors, water purification and drug delivery [31]. Several computational studies have also been conducted to study the properties of graphene such as semiempirical PM6 and DFT computational modeling of the adsorption of various molecules on the surface of graphene [32], semiempirical PM6 and DFT modeling of the interaction of bisphenol A with graphene and graphene oxide in adsorb state [33], and studying the adsorption/release of various pharmaceuticals on graphene and its derivatives using different quantum mechanical methods and molecular dynamics simulations [34]. However, based on our literature survey, there was no molecular modeling study conducted to comprehensively study the physical, electronic and thermal properties of G/CaO nanocomposites. Therefore, this work is conducted to study G/CaO nanocomposites using semiempirical PM6 method. Some properties including ionization potential, charge distribution, TDM and thermal parameters were calculated.

2. Calculation Details

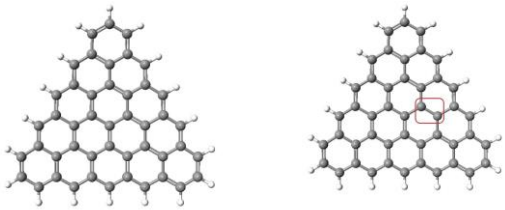
The studied models were calculated with SCIGRESS software [35] at Molecular Modeling and Spectroscopy Unit, Spectroscopy Department, National Research Centre, Egypt. Each structure was optimized to semiempirical level at PM6 [36] method to calculate the charge distribution and TDM. Second derivative was also calculated for the studied structures to ensure that each structure corresponding to energy minima as its infrared spectrum is positive. Then thermal parameters were calculated using the same level of PM6. All the parameters were calculated with CaO interacting with graphene once through O and once through Ca, in the form of both adsorb and complex states.

3. Results and Discussions

3.1. Building model molecules

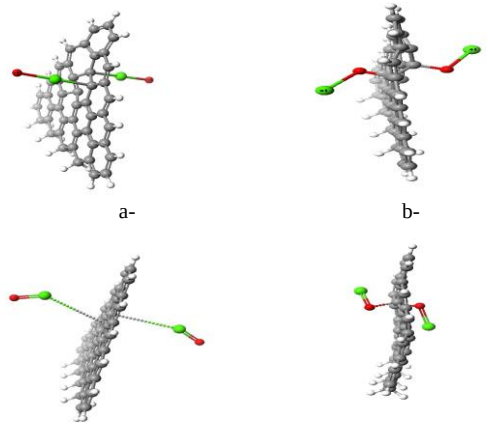
An important step before carrying out the calculations is to describe how to build the studied model molecules. Graphene model is indicated as a strip of 46 carbon atoms. Two metal oxide molecules were proposed to interact with two carbon atoms close to each other as one bond between these carbon atoms was broken as

indicated in figure 1. The metal oxide was supposed to interact once through the O atom and once through the metal's atom itself. Assuming that the interaction scheme is either physical (adsorb) or chemical (complex), then we have five models based on these assumptions; namely, graphene (G); G/2CaO as complex state ($G/2CaO_{comp}$); G/2CaO as adsorb state ($G/2CaO_{ads}$); G/2OCa as complex state ($G/2OCa_{comp}$) and G/2CaO as adsorb state ($G/2OCa_{ads}$). The model molecules are demonstrated in figures 1 and 2 respectively.



a- b-

Fig. 1. The studied model molecule of graphene which consists of 46 carbon atoms as indicated in (a), the labeled atoms indicated one of the C=C bond is broken to form C-C then 2CaO are interacted with graphene through these two atoms as indicated in (b).



a- b-

c- d-

Fig. 2. The studied four model molecules for graphene which were interacted as complex and adsorb state with 2CaO once through O then through Ca to form a- $G/2CaO_{comp}$, b- $G/2OCa_{comp}$, c- $G/2CaO_{ads}$ and d- $G/2OCa_{ads}$

3.2. Calculated Physical Parameters

Table 1 presents the PM6 calculated molecular weight, final heat of formation in Kcal, ionization potential in eV, and molecular point group for $G/2CaO_{comp}$ and $G/2OCa_{comp}$, and $G/2CaO_{ads}$ and $G/2OCa_{ads}$. The molecular weight of graphene was 570.6482, while after the interaction with CaO it increased to 686.8386, regardless of the type of interaction (adsorb or complex), and regardless of the molecule through which the interaction took place (O or Ca). Molecular point group was D3h corresponding to graphene and then changed to C1 after interaction with CaO, regardless of the type of interaction. The change in the molecular point group indicates that the graphene sheet used as a model molecule loses its symmetry a little bit as a result of forming a composite with CaO. As shown in figure 2 which demonstrates the optimized structure of the four model molecules for G/CaO, it is clear that there is some deformation as a result of the formation of the composite between graphene and CaO. The deformation is clear in all four studied model molecules. Consequently, the final heat of formation of the four model molecules was calculated in order to verify the stability of such composites. The final heat of formation is defined as the change in the enthalpy of a given structure during the formation of 1 mole of this structure from its constituent elements, with all the substances in their standard states [37]. As a general behavior, the final heat of formation is decreased as a result of the interaction between graphene and CaO. This decrease is much more noticeable with the interaction taking place through the Ca atom than through the O atom. The decrease in the final heat of formation of the studied composites reflects that the composites are thermally stable. Correlating this result with that of the symmetry, one can conclude that the studied composites are deformed, yet thermally stable. The calculated ionization potential was 6.4559 eV for graphene and remained almost unchanged in the adsorb state (6.3403 eV for G/CaO and 6.7785 eV for G/2OCa), but then increased to 9.9078 eV and 10.9435 eV for $G/2CaO_{comp}$ and $G/2OCa_{comp}$, respectively.

The TDM is one of the parameters closely related to the reactivity of a given structure. It was stated earlier that as the higher the TDM of the structure, the more reactive it becomes with its surrounding medium [38-39]. The calculated TDM was 1.274 Debye for graphene, but then increased to 7.346 Debye and 9.271 Debye for G/CaO_{ads} and G/OCaads, respectively. For $G/2CaO_{comp}$ and $G/2OCa_{comp}$, the TDM is further increased to 21.569 Debye and 7.111 Debye, respectively. This is an indication for the reactivity of the formed G/CaO composites in both adsorb and complex states.

Table 1. PM6 calculated Molecular weight, Molecular point group, final heat of formation (KCal), Ionization potential (eV), total dipole moment (Debye) for G/2CaO and G/2OCa as complex G/2CaO and G/2OCa as adsorb state.

		Adsorb state		Complex	
	G	**G/CaO**	**G/2OCa**	**G/2CaO**	**G/2OCa**
Molecular weight	570.6482	686.8386	686.8386	686.8386	686.8386
Point group	D3h	C1	C1	C1	C1
Final heat of formation	265.244	239.927	88.664	114.845	-6533.749
Ionization potential	6.4559	6.3403	6.7785	9.9078	10.9435
Total dipole moment	1.274	7.346	9.271	21.569	7.111

3.3. Calculated Charge Distributions

Another effect upon graphene as a result of composite formation with CaO is investigated by studying the charge transfer. Table 2 presents the PM6 calculated charge, number of electrons, s-Pop and p-Pop for $G/2CaO_{comp}$ and $G/2OCa_{comp}$, and $G/2CaO_{ads}$ and $G/2OCa_{ads}$. As shown in table 2, the parameters are corresponding to the two atoms at which one bond is broken then two molecules of CaO are interacted with graphene through them. Regarding graphene, the partial charge on the first atom was -0.032417 and the number of electrons was 4.0324, distributed as 1.08407 in s-Pop and 2.94835 in p-Pop. For the other carbon atom, the partial charge was 0.032116 and the number of electrons was 3.9679, distributed as 1.09544 in s-Pop and 2.87245 in p-Pop. As far as CaO is interacted with graphene in adsorb or complex state, this induced that the change in the partial charges depends on the change in the distribution of electrons. Correlating these data with the data in table 1, especially the TDM, indicates that the redistribution of electrons partially enhances the charge which in turn changes the TDM. Although this effect is physical, it still does have an effect on the reactivity of the composites being studied which is a chemical effect. In order to confirm the stability of the studied composites, another confirmation is needed. Accordingly, some thermal parameters are calculated and listed in table 3.

Table 2. PM6 calculated charge, number of electrons, s-Pop and p-Pop for G/2CaO and G/2OCa as complex G/2CaO and G/2OCa as adsorb state.

	Charge	**No. of electrons**	**s-Pop**	**p-Pop**
G	-0.032417	4.0324	1.08407	2.94835
	0.032116	3.9679	1.09544	2.87245
$G/2CaO_{comp}$	0.288501	3.7115	1.09353	2.61797
	-0.319519	4.3195	1.09685	3.22267
$G/2OCa_{comp}$	0.421020	3.5790	1.07852	2.50046
	0.298984	3.7010	1.10083	2.60018
G/CaO_{ads}	0.144532	3.8555	1.08716	2.76831
	-0.222393	4.2224	1.09136	3.13103
$G/2CaO_{ads}$	0.394684	3.6053	1.09922	2.50609
	0.363747	3.6363	1.10413	2.53212

Table 3. PM6 calculated enthalpy (Cal/Mole), heat capacity (Cal/K/Mol) and entropy (Cal/K/Mol) for $G/2CaO_{comp}$, $G/2OCa_{comp}$, $G/2CaO_{ads}$ and $G/2OCa_{ads}$

	Enthalpy, Cal/Mole	**Heat Capacity, Cal/K/Mol**	**Entropy, Cal/K/Mol**
G	18055.747	125.674	172.535
$G/2CaO_{comp}$	23286.922	148.011	223.510
$G/2OCa_{comp}$	22718.522	147.372	217.198
$G/2CaO_{ads}$	23427.971	146.167	240.409
$G/2OCa_{ads}$	22164.832	147.623	205.963

3.4. Calculated Thermal Parameters

Table 3 presents the PM6 calculated enthalpy in Cal/Mole, heat capacity in Cal/K/Mol and entropy in /K/Mol for G/2CaO$_{comp}$, G/2OCa$_{comp}$, G/2CaO$_{ads}$ and G/2OCa$_{ads}$. Enthalpy is a convenient state function preferred in many measurements in chemical, biological, and physical systems at a constant pressure. It is the sum of the system's internal energy and the product of its pressure and volume [40]. Entropy is the number of possible configurations of system's components that is consistent with the state of the system as a whole [41]. Heat capacity is a physical quantity which describes how much heat a substance must add to raise its temperature by 1 degree Celsius [42]. Comparing between the thermal parameters of graphene and the proposed composites confirms that thermal stability exists for the studied composites which is consequently a confirmation for the obtained results of the final heat of formation. The thermal parameters described in table 3 were consistent with the results of the final heat of formation. It is clear that the values of entropy, enthalpy and heat capacity for the composites are higher than those for graphene. This confirms that the studied composites are thermally stable.

4. Conclusion

The composite formation between graphene and CaO resulted in deformation of the structure of graphene, yet it became thermally stable. The calculated TDM values of the studied G/CaO composites were higher than that of graphene individually, indicating that the studied composites are more reactive that graphene itself. Although reactivity is a chemical effect, it is still coming from the change in the partial charges induced by the redistribution of electrons as a result of composite formation, concluding that the interaction of CaO with graphene caused the charge to be withdrawn then partially changed, which in turn changed the TDM and enhanced the reactivity of the G/CaO composite. Based on the obtained results, the present computational work gives an indication for the enhancement of the electronic properties of graphene as a result of interaction with CaO.

5. References

[1] Agudosi E.S., Abdullah E.C., Numan A., Mubarak N. M., Aid S. R., Benages-Vilau R., Gómez-Romero P., Khalid M., Omar N., Fabrication of 3D binder-free graphene NiO electrode for highly stable supercapattery. Scientific Reports, 10, 11214 (2020).

[2] Najib S., Erdem E., Current progress achieved in novel materials for supercapacitor electrodes: Mini review. Nanoscale Advances, 1, 2817–2827(2019).

[3] Shao H., Padmanathan N., McNulty D., O'Dwyer C., Razeeb K. M., Supercapattery based on binder-free Co3(PO4)2·8H2O multilayer nano/microflakes on nickel foam. ACS Applied Materials and Interfaces, 8, 28592–28598 (2016).

[4] Novoselov K. S., Geim A.K. , Morozov S.V. , Jiang D. , Zhang Y. , Dubonos S.V. , Grigorieva I.V., Firsov A.A. , Electric Field Effect in Atomically Thin Carbon Films. Science, 306, 666-669 (2004).

[5] Rusanov A.I. , Cohesive energy and line energy of graphene. Nanoscale, 6, 8130-8133 (2014).

[6] Sahu S. , Sahoo M.R. , Kushwaha A.K. , Rout G.C., Nayak S.K., Charge transfer and hybridization effect at the graphene-nickel interface: A tight binding model study. Carbon, 142, 685-696 (2019).

[7] Bolotin K.I. , Sikes K.J. , Jiang Z., Klima M. , Fudenberg G., Hone J. , Kim P., Stormer H.L. , Ultrahigh electron mobility in suspended graphene. Solid State Communications, 146, 351-355 (2008).

[8] Kim K.S. , Zhao Y. , Jang H. , Lee S.Y. , Kim J.M. , Kim K.S. , Ahn J.H. , Kim P. , Choi J.Y., Hong B.H. , Large-scale pattern growth of graphene films for stretchable transparent electrodes. Nature, 457, 706-710 (2009).

[9] Li X., Chen Y., Cheng Z. , Jia L., Mo S., Liu Z. , Ultrahigh specific surface area of graphene for eliminating subcooling of water. Applied Energy, 130, 824-829 (2014).

[10] George J.M. , Antony A. and Mathew B.J.M.A. , Metal oxide nanoparticles in electrochemical sensing and biosensing: a review. Microchimica Acta, 185, 358 (2018).

[11] Fadillah G., Saleh T.A., Wahyuningsih S., Enhanced electrochemical degradation of 4-Nitrophenol molecules using novel Ti/TiO2-NiO electrodes. Journal of Molecular Liquids, 289, 111108 (2019).

[12] Zhang H., Liu S., Nanoparticles-assembled NiO nanosheets templated by graphene oxide film for highly sensitive non-enzymatic glucose sensing. Sensors and Actuators B Chemical, 238, 788-794 (2017).

[13] Liu X., Yao Y., Ying Y., Ping J., Recent advances in nanomaterial-enabled screen-printed electrochemical sensors for heavy metal detection. TrAC Trends Analytical Chemistry, 115, 187-202 (2019).

[14] Kate R. S., Khalate S. A., Deokate R. J., Overview of nanostructured metal oxides and pure nickel oxide (NiO) electrodes for

supercapacitors: A review. Journal of Alloys and Compounds, 734, 89–111 (2018).
[15] Xiang Y., Yang Z., Wang Sh., Shahriar Md., Hossain A., Yu J., Kumar N. A., Yamauch Y., Pseudocapacitive behavior of the Fe2O3 anode and its contribution to high reversible capacity in lithium ion batteries. Nanoscale, 10, 18010–8018 (2018).
[16] Tang C., Li B.Q., Zhang Q., Zhu L., Wang H.F., Shi J.L., Wei F., CaO-templated growth of hierarchical porous graphene for high-power lithium-sulfur battery applications. Advanced Functional Materials, 26, 577-585 (2016).
[17] Chen W. Q. , Veksha A., Lisak G. , Graphene-like carbon nanosheets grown over alkali-earth metal oxides: Effects of chemical composition and physico-chemical properties. Carbon, 159, 378-389 (2020).
[18] Ibrahim M., Abd-El-Aal M., Spectroscopic study of the Interaction of Heavy Metals with Organic Acid. International Journal of Environment and Pollution, 35, 99-110(2008).
[19] Ibrahim M., Osman O., Spectroscopic Analyses of Cellulose: Fourier Transform Infrared and Molecular Modelling Study. Journal of Computational and Theoretical Nanoscience, 6, 1054–1058 (2009).
[20] Ibrahim M., Molecular Modelling and FTIR Study for K, Na, Ca and Mg Coordination with Organic Acid, Journal of Computational and Theoretical Nanoscience, 6, 682–685(2009).
[21] Omar A., Ezzat H., Elhaes H., Ibrahim M. A., Molecular Modeling Analyses for Modified Biopolymers, Biointerface Research in Applied Chemistry, 11, 7847-7859(2021).
[22] Abdelsalam H., Elhaes H., Ibrahim M. A., First principles study of edge carboxylated graphene quantum dots. Physica B, 537, 77-86 (2018).
[23] Ibrahim M. A., Elhaes H., El-Khodary S. A., Morsy M., Refaat A., Yahia I. S., Zahran H. Y., Molecular Modeling Analyses for the Effect of Alkali Metal Oxides on Graphene. Biointerface Research in Applied Chemistry. 8, 3522-3525 (2018).
[24] Abdelsalam H., Teleb N.H., Yahia I.S., Zahran H.Y., Elhaes H., Ibrahim M.A., First principles study of the adsorption of hydrated heavy metals on graphene quantum dot. Journal of Physics and Chemistry of Solids, 130, 32-40(2019).
[25] Ezzat H., Badry R., Yahia I.S., Zahran H.Y., Ibrahim A., Elhaes H., Ibrahim M.A., Mapping the molecular electrostatic potential of fullerene, Egyptian Journal of Chemistry, 6, 1391-1402 (2019).
[26] Al-Bagawi A. H., Bayoumy A. M., Ibrahim M. A., Molecular Modeling Analyses for Graphene Functionalized with Fe3O4 and NiO. Heliyon, 6, e04456 (2020).
[27] Badry R., Radwan S. H., Ezzat D., Ezzat H., Elhaes H., Ibrahim M., Study of the Electronic Properties of Graphene Oxide/(PANi/Teflon). Biointerface Research in Applied Chemistry. 10, 6926 – 6935 (2020).
[28] Bayoumy A. M., Refaat A., Yahia I. S., Zahran H. Y., Elhaes H., Ibrahim M. A., Shkir Mohd., Functionalization of Graphene Quantum Dots (GQDs) with Chitosan Biopolymer for Biophysical Applications. Optical and Quantum Electronics, 52, 16 (2020).
[29] Li M., Xiong P., Yan F., Li S., Ren C., Yin Z., Li A., Li H., Ji X., Zheng Y., Cheng Y., An overview of graphene-based hydroxyapatite composites for orthopedic applications. Bioactive Materials, 3, 1-18 (2018).
[30] Handayani M., Sulistiyono E., Rokhmanto F., Darsono N., Fransisca P. L., Erryani A., Wardono J. T., Fabrication of Graphene Oxide/Calcium Carbonate/Chitosan Nanocomposite Film with Enhanced Mechanical Properties. IOP Conf. Series: Materials Science and Engineering, 578, 012073 (2019).
[31] Khan M., Tahir M. N., Adil S. F., Khan H. U., Siddiqui M. R. H., Al-warthan A. A., Tremel W., Graphene based metal and metal oxide nanocomposites: synthesis, properties and their applications. Journal of Materials Chemistry A, 3, 18753–18808 (2015).
[32] Gordeev E. G., Polynski M. V., Ananikov V. P., Fast and accurate computational modeling of adsorption on graphene: a dispersion interaction challenge. Physical Chemistry Chemical Physics, 15, 18815-18821 (2013).
[33] Cortés-Arriagada D., Sanhueza L., Santander-Nelli M., Modeling the physisorption of bisphenol A on graphene and graphene oxide. Journal of Molecular Modeling, 19, 3569–3580 (2013).
[34] Veclani D., Tolazzi M., Melchior A., Molecular Interpretation of Pharmaceuticals' Adsorption on Carbon Nanomaterials: Theory Meets Experiments. Processes, 8, 642 (2020).
[35] MO-G Version 1.1A, Fujitsu Limited, Tokyo, Japan (2008).
[36] Stewart J. J. P., Optimization of parameters for semiempirical methods V: Modification of NDDO approximations and application to 70 elements. Journal of Molecular Modeling, 13, 1173-1213 (2007).
[37] IUPAC, Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"), 1997. Online corrected version: "standard pressure"(2006).
[38] Ibrahim M., Elhaes H., Computational Spectroscopic Study of Copper, Cadmium, Lead and Zinc Interactions in the Environment. International Journal of Environment and Pollution, 23, 417-424 (2005).
[39] Ibrahim M., Mahmoud A-A., Computational Notes on the Reactivity of Some Functional Groups. Journal of Computational and Theoretical Nanoscience, 6, 1523-1526 (2009).
[40] "Oxford Living Dictionaries". Archived from the original on 2016-08-17. Retrieved 2018-02-19.
[41] Ligrone, Roberto. "Glossary". Biological Innovations that Built the World: A Four-billion-year Journey through Life & Earth History. Entropy. Springer, p. 478 (2019).
[42] David H., Resnick, Robert . Fundamentals of Physics, Wiley, 524(2013).