Molecular orientation dependent divergence into electro-chemical sensing performance of Pd decorated ZnO nanosheets during guanine adsorption: a comparative analysis

Indranil Maity[1*], *Subhradeep* Hazra [2], and *Aheli* Majumdar [2]

[1]Associate Professor, Department of Electronics and Communication Engineering (ECE), Institute of Engineering and Management (IEM), University of Engineering and Management (UEM), Kolkata, West Bengal, India
[2]Student, Department of Electronics and Communication Engineering (ECE), Institute of Engineering and Management (IEM), Kolkata, West Bengal, India

Abstract. In the present study the variation of different electro-chemical properties was compared, such as the molecular electrostatic potential (MEP), the highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO), for the sensing of guanine molecule on palladium (Pd) doped ZnO nanosheet, in four different orientations, through first principle-based computations in Gaussian 09W and GaussView 6.0 software. After structural optimizations, the guanine molecule was observed over the Pd-doped ZnO nanosheet in four different orientations (with tilt angles), parallel to the ZnO nanosheet horizontal plane. It was found that in System-A (first case), the guanine molecule was nearly tilted by 10˚, with an adsorption energy of -0.257 eV, and binding distance of 3.33 Å, for System-B (second case), the same guanine molecule was tilted by almost 50˚ with an adsorption energy of -0.425 eV, and binding distance of 2.29 Å, whereas for System-C (third case) and System-D (fourth case), the adsorption energy, binding distance, and tilt angle was -0.402 eV, 2.29 Å, 120˚, and -0.282 eV, 2.37 Å, 150˚, respectively over Pd-doped ZnO nanosheet sensing element.

1 Introduction

Deoxyribonucleic acid (DNA) is a rudimentary molecule that stores genetic information and stimulates protein synthesis. It is a double-helix structure, having two strands coiled around each other, consisting of nucleotides, which can be categorized as purine bases (i.e., adenine and guanine) and pyrimidine bases (i.e., cytosine and thymine) [1]. Guanine is a planar molecule with a fused ring structure consisting of a five-membered imidazole ring and a six-membered pyrimidine ring. This aromatic compound has a molecular weight of 151.13 g/mol and a density of approximately 2.2 g/cm³. The significance of guanine in genetic coding and

* Corresponding author: indrasanu026@gmail.com

metabolic processes lead to a vibrant research field in an interdisciplinary manner [2]. Guanine, being present in the DNA sequence, has a special importance and, if left defective, it causes some kind of hindrance in cellular signaling and metabolism.

ZnO nanosheets consist of hexagonal wurtzite structures with a wide bandgap of about 3.37 eV. Due to their promising photocatalytic properties, these nanosheets are used to develop reactive surfaces for UV photodetectors, sensors, and environmental remediation [3]. The versatile characteristics of ZnO nanosheets make them highly selective for practical sensing and research purposes due to their distinctive optical and surface nature [4]. In the pristine ZnO nanosheet, palladium (Pd) was added as a dopant to increase the electron transition on the surface. Generally, when this noble metal is used as a nanoparticle, the catalytic activity of this surface modifier is triggered by electronic and chemical sensitization, which also holds true for our study. This catalytic activity enhances the dissociation and spillover of the target species, improving sensitivity [5]. This modified nanosheet was used in this research as a sensing surface.

The performance metrics of ZnO nanotube-based alcohol sensors were thoroughly compared by Maity et al. based on stability, sensitivity, and reaction time, focusing on hybridization with palladium (Pd) and reduced graphene oxide (rGO) [5]. Mao et al. reported an in-depth electrochemical analysis of the detection of guanine and adenine using nanocomposites of gold-platinum nanoclusters and reduced graphene oxide (AuPt NCs-rGO) in a neutral pH environment [6]. The use of graphene and hexagonal boron nitride (hBN)-based nanostructures was thoroughly explored by Rani et al. for the detection of all the nitrogenous bases present in DNA or RNA, through demonstration of the nanosensor's high sensitivity and selectivity towards biomolecules [7]. Emran et al. designed a highly active electrochemical sensor for the sensing and monitoring of guanine released from hydrolysed DNA, and exposed to oxidative stresses on DNA, utilizing S-doped carbon [8]. The adsorption of guanine, adenine, thymine, and cytosine on a zinc oxide-decorated graphene sheet was analyzed and compared to a standard graphene sheet by Manesh et al. using Density Functional Theory (DFT) based calculations [9]. Ana Maria Oliveira-Brett and Ana-Maria Chiorcea-Paquim provided a robust synopsis of nanostructured materials (NsM) modified electrochemical sensors to detect 8-oxoguanine (8-oxoG) and its corresponding nucleotide, 8-oxo-2′-deoxyguanosine (8-oxodG), based on fundamental principles of electroanalysis [10]. In addition to this, Rahman Hallaja and Abdollah Salimi revealed the particulars of the catalytic oxidation of guanine using a glassy carbon electrode modified with an easily prepared cobalt oxide nanostructure [11]. Ortmann et al. described the impact of water molecules within the guanine crystal and their influence on the structural, vibrational, and electrical properties, using the first principles DFT study [12].

In this research study, a thorough analysis of the electro-chemical properties such as molecular electrostatic potential (MEP), and molecular orbitals (MOs) was done for four different orientations of guanine over Pd-doped ZnO nanosheet during the sensing. The research focused on determining how the angular orientation of the analyte/test molecule affects the sensitivity and selectivity of the sensing material towards it.

2 Computational Details

In this research, all the computational calculations were carried out using the first principle-based semi-empirical methods in the Gaussian 09W and GaussView 6.0 software. The analyzed structures for the four systems considered were optimized with a ZDO basis set. Given that the total number of electrons in all the systems was 1024, the spin-restricted PM6 function was employed for optimization which is useful in modelling and studying molecules, particularly those having biochemical interest, having an ability to predict molecular properties accurately [13].

In this study, at first, guanine was placed parallel to the Pd-decorated ZnO nanosheet in different positions before the optimization. Using the aforementioned method, after optimization, four types of systems were generated viz. System-A: Guanine adsorbed Pd-ZnO nanosheet with nearly 10˚ tiltation, System-B: Guanine adsorbed Pd-ZnO nanosheet with close to a tilt angle of 50˚, System-C: Guanine adsorbed Pd-ZnO nanosheet at a tilt angle of 120˚, and lastly, System-D: Guanine adsorbed Pd-ZnO nanosheet with almost a tilt angle of 150˚.

Adsorption energy is a key parameter to determine the sensing ability of the sensing material. So, the adsorption energy ($E_{Adsorption}$) was calculated using the following equation [14]:

$$E_{Adsorption} = E_{whole\text{-}system} - (E_{Guanine} + E_{Pd\text{-}ZnO\ sheet}) \quad (1)$$

where, $E_{whole\text{-}system}$ was the total electronic energy of all four systems with adsorption of guanine species and $E_{Pd\text{-}ZnO\ sheet}$ was the individual electronic energy of palladium doped ZnO nanosheets without adsorption of the analyte. Lastly, $E_{Guanine}$ was the electronic energy of the guanine molecule individually [14].

3 Results and Discussion

3.1 Adsorption Energy and Binding Distance:

Adsorption energy is a dominant parameter of surface chemistry to calculate the strength of the interaction between Pd-decorated ZnO nanosheet and guanine. Binding distance is the shortest distance between the nanosheet and the guanine molecule.

Table 1. Adsorption energy and binding distance of all systems for guanine sensing onto Pd-decorated ZnO nanosheet

Parameters	**System-A (tilt angle = 10˚)**	**System-B (tilt angle = 50˚)**	**System-C (tilt angle = 120˚)**	**System-D (tilt angle = 150˚)**
Adsorption Energy (eV)	-0.257	-0.425	-0.402	-0.282
Binding Distance (Å)	3.33	2.29	2.29	2.37

In the current study, adsorption energy and binding distance were critically examined using equation (1), with results documented in Table 1. It was found that System-B, where the tilt angle was 50˚, exhibited the highest adsorption energy and the lowest binding distance, due to the presence of more amount of Van der Waals force of attraction, as shown in Fig. 1. Since $E_{Adsorption\ (System\text{-}A)} < E_{Adsorption\ (System\text{-}D)} < E_{Adsorption\ (System\text{-}C)} < E_{Adsorption\ (System\text{-}B)}$, it can be concluded that System-B would be more stable.

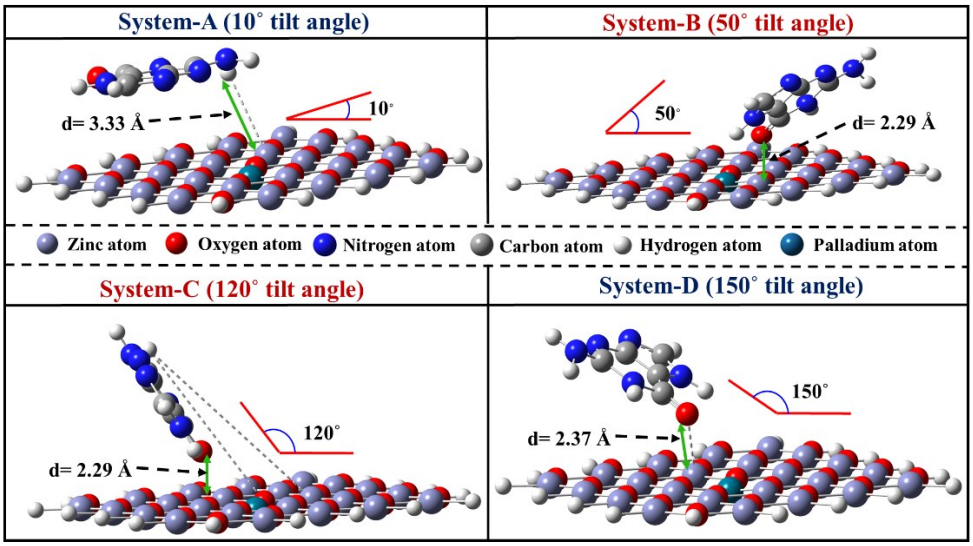

Fig. 1. Optimized structures of all four examined systems where the tilt angles were 10˚, 50˚, 120˚, and 150˚

3.2 Analysis of molecular orbitals (MOs):

With the assistance of molecular orbital analysis, it is feasible to identify the positions of the highest occupied and the lowest unoccupied molecular orbital (HOMO and LUMO, respectively) regions along with their energy levels in a system. The HOMO-LUMO energy gap indicates the chemical response of the system [15].

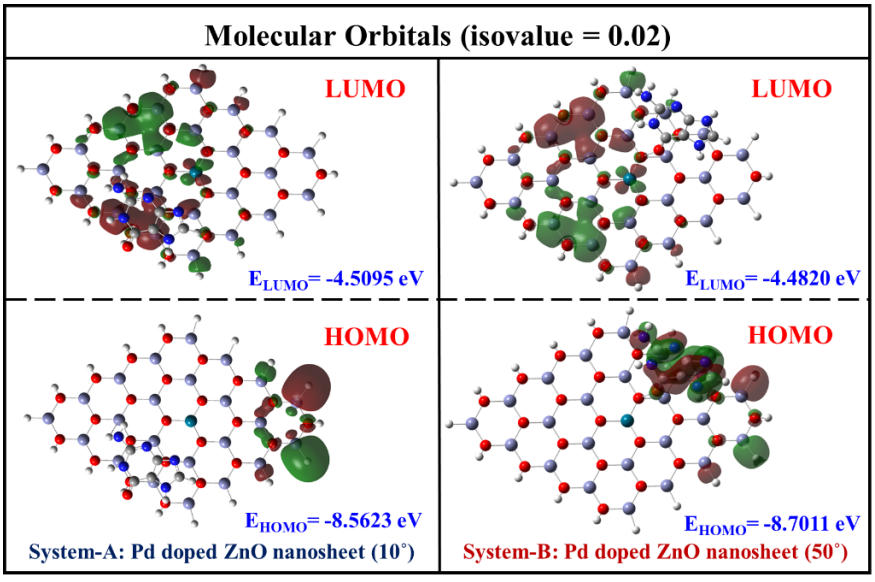

Fig. 2. Molecular orbitals analysis of System-A (tilt angle =10˚), and System-B (tilt angle =50˚)

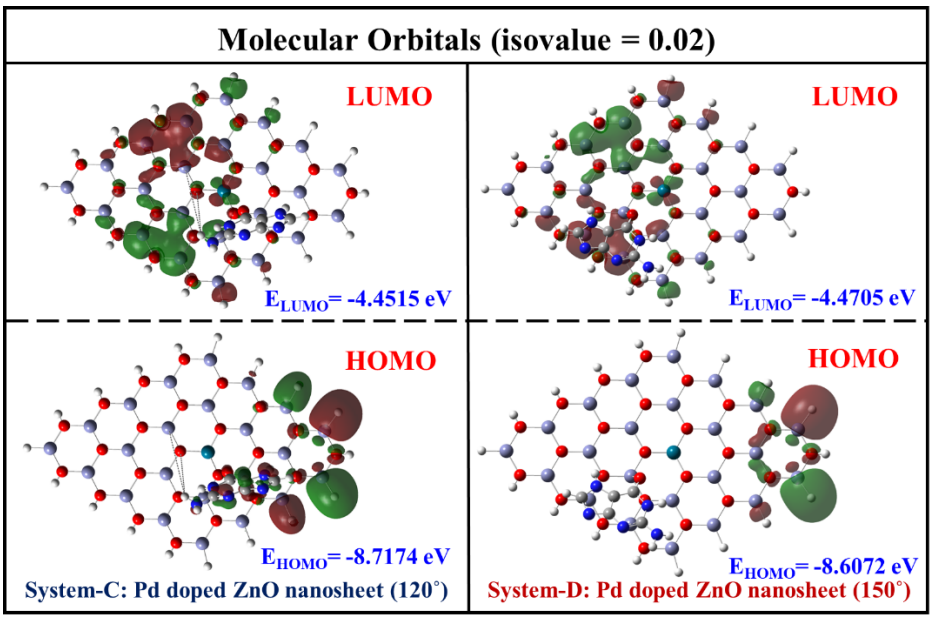

Fig. 3. Molecular orbitals analysis of System-C (tilt angle =120˚), and System-D (tilt angle =150˚)

In the given Fig. 2 and Fig. 3, the regions of the HOMO and LUMO were shown for each system with their corresponding energy value. Additionally, in the following Table 2, the HOMO-LUMO energy gap was calculated for each system. From these results, it can be observed that System-A was less stable and more responsive due to relatively low excitation energy [5].

Table 2. HOMO-LUMO energy gap of four examined cases

Parameters	**System-A (tilt angle = 10˚)**	**System-B (tilt angle = 50˚)**	**System-C (tilt angle = 120˚)**	**System-D (tilt angle = 150˚)**
E_{HOMO} (eV)	-8.5623	-8.7011	-8.7174	-8.6072
E_{LUMO} (eV)	-4.5095	-4.4820	-4.4515	-4.4705
$E_{HOMO-LUMO}$ gap (eV)	4.0528	4.2191	4.2659	4.1367

3.3 Visualization of molecular electrostatic potential (MEP) mapping:

Molecular electrostatic potential (MEP) is an electronic characteristic that describes the charge distribution within the system, offering insights into molecular reactivity and potential interaction sites [5].

In this study, MEP mapping was produced using the Self-Consistent Field (SCF) method. The three-dimensional maps were plotted within a potential range of -6.143e0 eV (represented in dark red) to -2.255e0 eV (represented in dark blue), with an isovalue set at 0.0004. In the MEP maps, the nucleophilic regions were represented by red, electrophilic centers were represented by blue, and the neutral areas were highlighted by green. In all four

cases shown in Fig. 4, the binding point of guanine on the ZnO nanosheet had the largest negative potential, whereas the potential increased towards the hydrogen-passivated edges, following the color gradient: blue > green > yellow > orange > red.

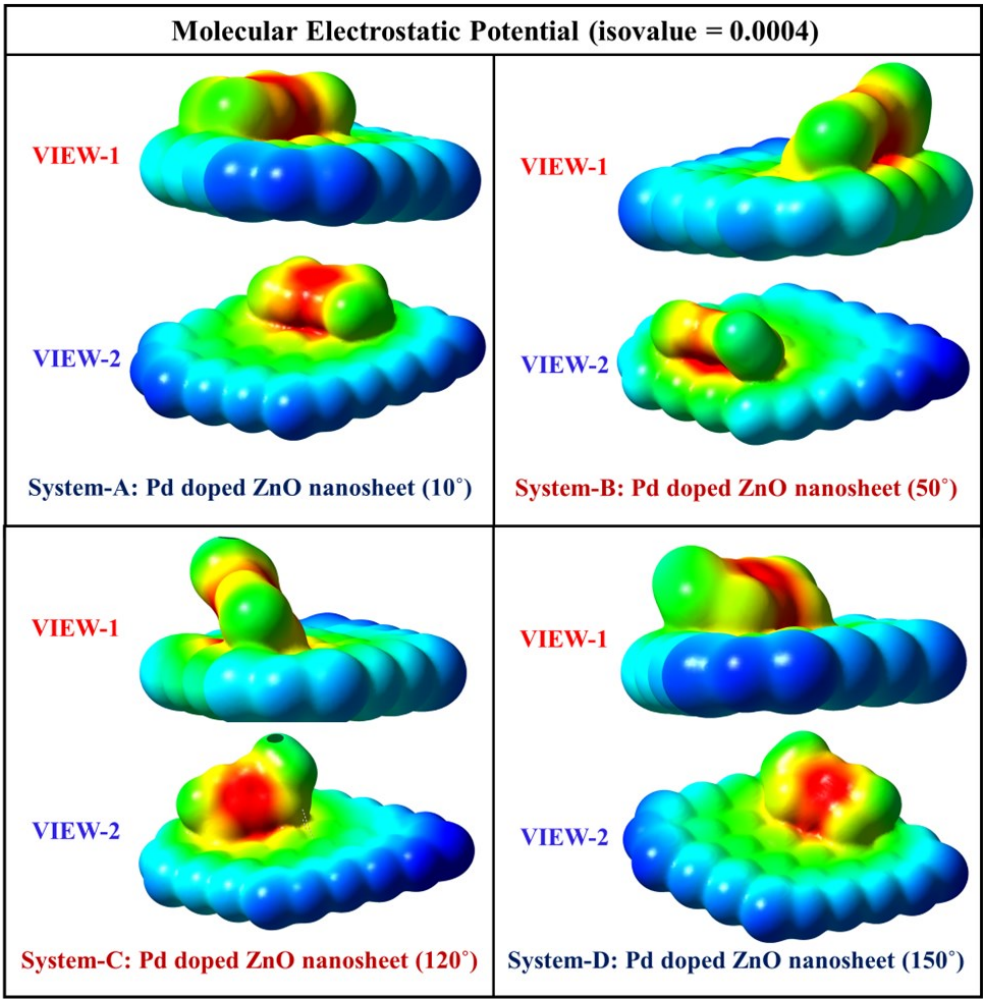

Fig. 4. MEP mapping of System-A (10˚ tilt angle), System-B (50˚ tilt angle), System-C (120˚ tilt angle), and System-D (150˚ tilt angle)

4 Conclusion

This research investigation focused on the first principle calculation technique and critically compared the sensing ability of Pd-decorated ZnO nanosheets for detecting guanine (based on their orientation). The study thoroughly reviewed various electro-chemical parameters, including molecular orbital (MO) analysis, and molecular electrostatic potential (MEP), providing a detailed comparison of the four proposed systems. The analysis revealed that System-B exhibited maximum adsorption with an adsorption energy of -0.425 eV which was almost 1.7 times, compared to System-A exhibiting the least adsorption with an adorption energy of -0.257 eV. This could be inferred from the adsorption distance which gradually

decreased in System-B and System-C, therefore bringing the guanine molecule closer to the sensing surface, supporting the reason for the increase in adsorption between the adsorbate and sensing material. The study put forward that Pd-doped ZnO nanosheets are effective biosensors for detecting guanine analyte at an angle of 50˚ and 120˚, relative to the sensor surface, which has substantial significance for biochemical applications.

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References

1. W. Saenger, Structures and conformational properties of bases, furanose sugars, and phosphate groups, (Principles of Nucleic Acid Structure. Springer Advanced Texts in Chemistry. Springer, 1984)
2. K. Chetankumar, B. E. Kumara Swamy, and H. S. Bhojya Naik, MgO and MWCNTs amplified electrochemical sensor for guanine, adenine and epinephrine. Materials Chemistry and Physics 267, 124610 (2021).
   https://doi.org/10.1016/j.matchemphys.2021.124610
3. R. Tayebee, and A. H. Nasr, Studying adsorption and detoxification of sulphur mustard chemical warfare onto ZnO nanostructures. Journal of Molecular Liquids 319, 114357 (2020).
   https://doi.org/10.1016/j.molliq.2020.114357
4. B. Ul Haq, S. AlFaify, T. A. Alrebdi, R. Ahmed, S. Al-Qaisi, M. F. M. Taib, G. Naz, S. Zahra, Investigations of optoelectronic properties of novel ZnO monolayers: A first principles study. Materials Science and Engineering: B 265 (2021).
   https://doi.org/10.1016/j.mseb.2021.115043
5. I. Maity, D. Acharya, K. Huang, P. Chung, M. Ho, and P. Bhattacharyya, A comparative study on performance improvement of ZnO nanotubes based alcohol sensor devices by Pd and rGO hybridization. IEEE Trans. Electron Dev. 65 (2018).
   10.1109/TED.2018.2846784
6. B. Mao, L. Qian, M. Govindhan, Z. Liu, and A. Chen, Simultaneous electrochemical detection of guanine and adenine using reduced graphene oxide decorated with AuPt nanoclusters. Microchimica Acta 188, 276 (2021).
   https://doi.org/10.1007/s00604-021-04926-7
7. S. Rani, and S. J. Ray, DNA and RNA detection using graphene and hexagonal boron nitride based nanosensor. Carbon 173 (2021).
   https://doi.org/10.1016/j.carbon.2020.06.061
8. M. Y. Emran, M. A. Shenashen, S. A. El-Safty, and M. M. Selim, Design of porous S-doped carbon nanostructured electrode sensor for sensitive and selective detection of guanine from DNA samples. Microporous and Mesoporous Materials 320, 111097 (2021).
   https://doi.org/10.1016/j.micromeso.2021.111097

9. E. M. Manesh and M. M. Mahdevar, Adsorption behavior of guanine, adenine, thymine, and cytosine nucleobases of DNA on zinc oxide-graphene nanosensor: A DFT study. Synthetic Metals 267 (2020).
https://doi.org/10.1016/j.synthmet.2020.116486
10. A. Chiorcea-Paquim and A. M. Oliveira-Brett, Nanostructured material–based electrochemical sensing of oxidative DNA damage biomarkers 8-oxoguanine and 8-oxodeoxyguanosine: a comprehensive review. Microchimica Acta 188, 58 (2021).
https://doi.org/10.1007/s00604-020-04689-7
11. R. Hallaja, and A. Salimi, Nanomolar detection of guanine based on a novel cobalt oxide nanostructure-modified glassy carbon electrode. Analytical Methods 3 (2011).
https://doi.org/10.1039/C0AY00675K
12. F. Ortmann, K. Hannewald, and F. Bechstedt, Guanine Crystals: A first principles study. J. Phys. Chem. B 112, 5 (2008).
https://pubs.acs.org/doi/abs/10.1021/jp076455t
13. M. Kamel, H. Raissi, H. Hashemzadeh, and K. Mohammadifard, Theoretical elucidation of the amino acid interaction with graphene and functionalized graphene nanosheets: insights from DFT calculation and MD simulation. Amino Acids 52 (2020).
https://doi.org/10.1007/s00726-020-02905-5
14. I. Maity, S. Das, M. Gangopadhyay, and I. Maity, Understanding 2-propanol sensing mechanism of Pd modified graphene based gas sensor devices using DFT study, in Proceedings of the 37th International Conference on VLSI Design and 23rd International Conference on Embedded Systems (VLSID), Kolkata, India, January 06-10 (2024).
https://doi.org/10.1109/vlsid60093.2024.00011
15. P. Lakhera, S. Singh, R. Mehla, V. Chaudhary, P. Kumar, and S. Kumar, Boronic acid decorated graphene nano flakes for glucose sensing in diabetes: a DFT prediction. IEEE Sensors Journal 22 (2022).
10.1109/JSEN.2022.3158003