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# Investigation of the Interaction between Indium Oxide Cluster and a Water Molecule via Density Functional Theory

Nisreen A. Fejer[1,2,*], Mohammed T. Hussein[3,4], Asmaa H. Mohammed[2]

[1] Department of Physics, College of Science for Women, Baghdad University, Baghdad, Iraq.
[2] College of Science, Al-Nahrain University, Jadiriya, Baghdad, Iraq
[3] College of Science, Baghdad University, Baghdad, Iraq
[4] AlNukhba University College, Baghdad, Iraq

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**Abstract**

Density Functional Theory (DFT), with a hybrid function B3LYP, has continued to be considered an adequate computational methodology for evaluating the interaction between indium oxide ($In_{10}O_{15}$) pyramid nanoclusters and water. This computation evaluated the light atoms (O and H) with the 6-311G ** basis set, while the heavier indium atoms were treated with the Stuttgart/Dresden (SDD) basis set. HOMO, LUMO molecular orbital electronic structure, and energy gap, as well as geometrical structure, were computed in Gaussian 09W and GaussView 05, respectively. It was found that the energy gap of $In_{10}O_{15}$ increases in the presence of water, which means water uptake would reduce the electrical conductivity of the indium oxide nanocluster. While the Gibbs free energy was found to be a positive value, $\Delta G \approx 2.9$ eV, which means the reaction is endergonic. This transformation is associated with an energetically favorable electron transition, which may involve photocatalytic activity.

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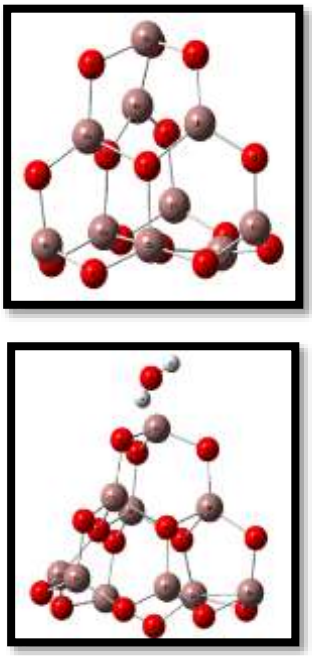
*Corresponding author: nisreen@csw.uobaghdad.edu.iq

## 1. Introduction

Due to its remarkable physical and chemical properties, including high optical transparency and electrical conductivity, indium oxide ($In_2O_3$) is an important oxide in various technological applications, such as solar cells, optoelectronics, and gas sensors. Recent studies have shown that reducing the crystal size of such materials to the nanoscale is accompanied by significant changes in their surface and electronic properties, thereby opening new avenues for their use in highly sensitive and precise devices. At the nanoscale, the surface-to-volume ratio increases significantly, underscoring the vital need to investigate surface interactions with ambient molecules, including water molecules. [1-13]. Powerful approaches have been created with the development of quantum computing techniques and solid-state theories called first-principles methods, primarily among Density Functional Theory (DFT). One of the most important techniques for studying the electrical structures and chemical interactions of solids and molecules has been DFT. This theory has allowed for an exact description of the electron density distribution, enabling better knowledge of electronic transitions, adsorption processes, and chemical reactions on nanoscale surfaces. Moreover, reaction rates and related energy barriers are computed using supplementary methods such as Transition State Theory (TST). [14-17]. These ideas have been widely used in recent years to investigate the interaction of nanomaterials with basic molecules, particularly water molecules, thereby creating very sensitive humidity sensors. However, results from experiments in this area have often been conflicting or inconsistent. This scenario emphasizes the importance of the current work, which seeks to explore the interaction between a nanocluster of indium oxide and a water molecule using the Density Functional Theory (DFT) technique. Apart from estimating the transition rate using the Transition State approach, the study is focused on examining variations in the electronic structure and adsorption energy levels to evaluate the efficacy of this system as a humidity sensor. [18-25].

## 2. Methodology

Density Functional Theory (DFT) has been widely recognized as one of the most effective computational approaches for investigating nanostructured materials' structural and electronic properties. Its ability to closely approximate experimental observations has made it particularly advantageous for theoretical studies. The hybrid functional B3LYP (Becke level-3 parameters, Lee-Yang-Parr), which combines Hartree-Fock exchange with exchange-correlation functional derived from various sources, has been employed in the present work. Due to its balanced accuracy and computational efficiency, the hybrid functional has remained one of the most frequently used functionals in quantum chemical simulations. For the basis sets, the 6-311G ** basis has been utilized for light atoms such as hydrogen (H) and oxygen (O). At the same time, the Stuttgart/Dresden (SDD) effective core potential has been adopted for the heavier indium (In) atoms. Geometric optimizations and electronic structure calculations were carried out using the Gaussian 09W software package [26]. Two molecular systems were considered: the isolated indium oxide nanocluster ($In_{10}O_{15}$) and its complex with a water molecule ($In_{10}O_{15}$ + $H_2O$). The optimized geometries for both systems are illustrated in Figure 1. These geometries were obtained through full geometry optimization using Gaussian View 05 [27-31].


(a)

(b)

Figure 1. Geometrical optimization of (a) $In_{10}O_{15}$ (b) $In_{10}O_{15}$ with water.

To elucidate the interaction between the $In_{10}O_{15}$ nanocluster and the water molecule, a set of reaction pathways was proposed and examined, as described by the following equations:

$$[In_{10}O_{15}\ H_2O]^{A} \rightarrow [In10O_{15}.H_2O]^{\dagger\dagger}\quad (\Delta G=0.29\ eV) \quad (1)$$
$$[In_{10}O_{15}\ H_2O]^{A} \rightarrow In_{10}O_{16} + H_2 \quad (\Delta G=2.9\ eV) \quad (2)$$
$$H_2O \rightarrow OH^{-} + H^{+} \quad (\Delta G=18.03\ eV) \quad (3)$$
$$H_2O \rightarrow H_2 + {}_{1/2}\ O_2 \quad (\Delta G=2.83\ eV) \quad (4)$$

Equations 1 and 2 have been shown to indicate that the interaction between $In_{10}O_{15}$ and $H_2O$ is characterized as a dipole-dipole adsorption interaction, followed by the formation of the transition state. The dipole-dipole interaction was attributed to the negative and positive charges of $H_2O$ and indium oxide atoms. This transformation has been associated with a positive Gibbs free energy change (AG = 2.9 eV), which is considered consistent with an energetically favorable electron transition, typically associated with photocatalytic activity. Equations 3 and 4 were used to provide the probability of water analysis, and Equation 4 was shown to be more stable thermodynamically.

## 3. Result and Discussion

### 3.1. Electronic Properties of Indium oxide and Indium Dioxide with water

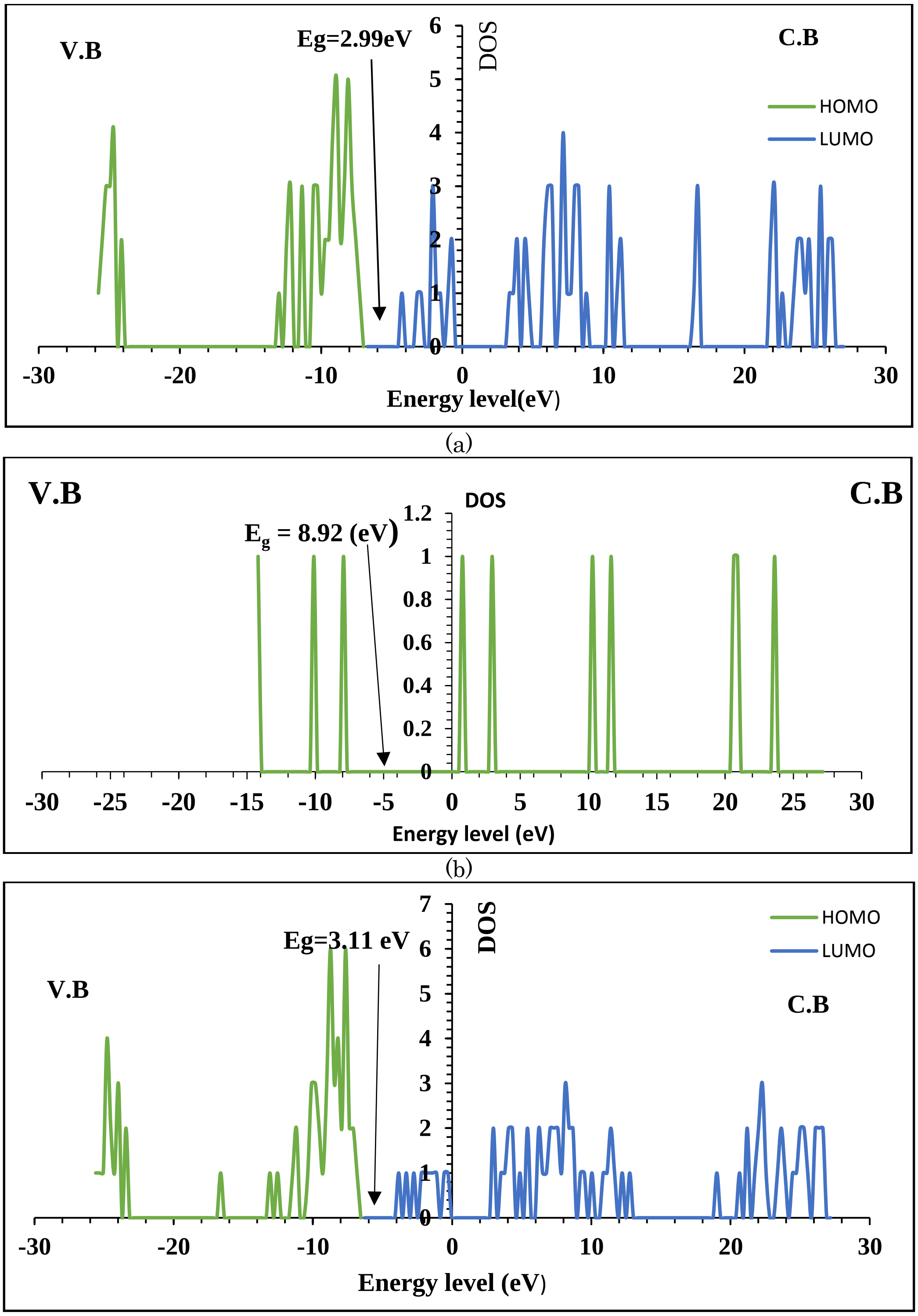
#### 3.1.1. Energy Gap

A fundamental electronic property of materials is the energy gap, defined as the variation in energy between the HOMO "higher occupied molecular orbital" and the LUMO "lower unoccupied molecular orbital" as shown in equation (5) . The band gap is essential in defining the electrical and optical characteristics of semiconductors and insulators. In nanoscale systems, surface effects can significantly influence the LUMO levels more than the HOMO levels, which in turn affects the overall band gap [32, 33].

$$Eg = / \text{First}(\text{LUMO}) - \text{Last}(\text{HOMO}) \ / \quad (5)$$

#### 3.1.2. Density of State (DOS) of Indium Dioxide

The density of states (DOS) is referred to as the quantity of states inside a system, specifically the number of electron states per unit volume per energy. Figure 2 illustrates the density of states for water ($H_2O$) and indium oxide ($In_{10}O_{15}$) as an indicator of energy levels subsequent to geometric optimization. The energy gap between the HOMO and LUMO, i.e., the valence band and conduction band, has been calculated. The energy gap of $In_{10}O_{15}$ was found to be 2.99 eV, which is considered to be in excellent agreement with the literature [1], and with the presence of water, it was increased to 3.11 eV. The increase in the energy gap has resulted in a rise in resistivity and a decrease in conductivity [34].



(a)

(b)

(c)

Figure 2. Density of the state of (a) $In_{10}O_{15}$, (b) $H_2O$, and (c)$In_{10}O_{15}$ with water.

### 3.2. Thermal Properties

### 3.2.1. Transition State

The chemical reaction's transition state is considered a special arrangement concerning the reaction path. It is defined as the stage with the highest potential energy. The total Gibbs free energy of activation within the reaction path is located at the activated state; see Figure 3. The energy level of the final state's product was greater than that of the reactants of the initial state of the reactions in Equation 1.

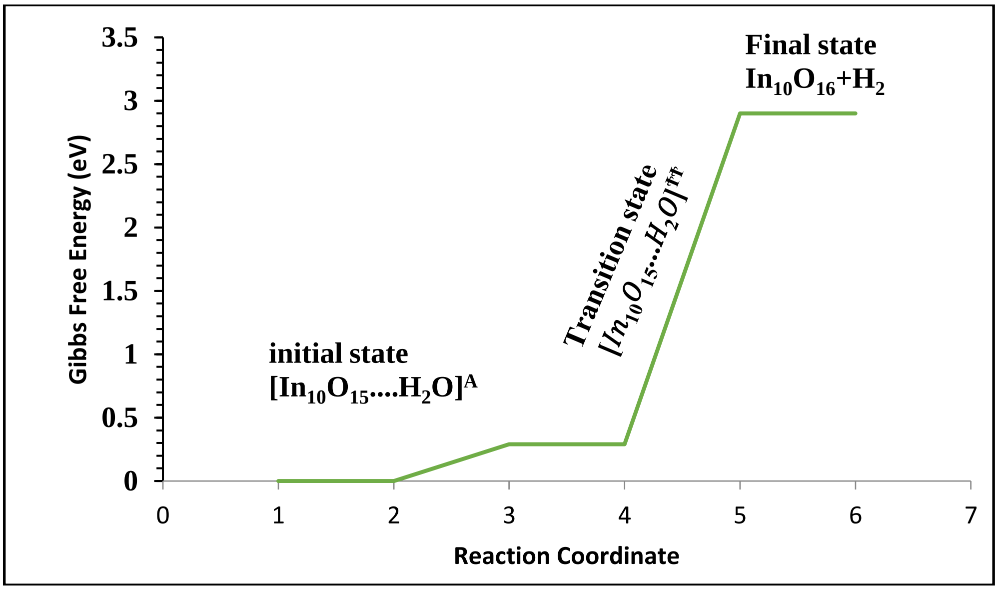


Figure 3. Gibbs free energy transition state process of the $In_{10}O_{15}$ cluster with the water molecule.

Figure 3 illustrates the Gibbs free energy profile for the water activation and splitting reaction on the $In_{10}O_{15}$ cluster. A significant increase in Gibbs free energy was observed at the transition state, indicating the presence of a substantial energy barrier that must be overcome for the reaction to proceed. This energy peak was reflected as the unstable, high-energy configuration of the system during the transformation [35, 36]. The final state, corresponding to the formation of $In_{10}O_{16}$ and $H_2$ molecules, displays a higher Gibbs energy than the initial state, suggesting that the overall process is considered endergonic, as shown in Equation 6.

$$\Delta G = \Delta H\text{-}T\Delta S \tag{6}$$

This thermodynamic behavior suggests that the process is non-spontaneous under ordinary circumstances and needs outside energy input, including thermal or photonic activation. [37]. Including an extra oxygen atom into the indium oxide lattice and releasing hydrogen gas, both of which are shown to change the system's entropy and enthalpy components, are mainly responsible for the rise in Gibbs energy [30]. Such knowledge is essential for grasping indium oxide-based materials' surface reactivity and catalytic capability in gas-sensing or water-splitting applications. The higher energy barrier is especially underlined, as it underlines the need to maximize the catalyst surface or add dopants to lower the activation energy, thereby improving the efficiency of the material in practical uses.

Table 1. Gibbs free energies for reactions and activations for both room temperature and atmospheric pressure, as well as their components (enthalpy and entropy)

| n | Reaction | ΔG(eV) | ΔH(eV) | TΔS(eV) |
|---|---|---|---|---|
| 1 | $[In_{10}O_{15}...H_2O]^A \rightarrow [In10O15H2O]^{\dagger}$ † | 0.29 | 0.21 | -0.08 |
| 2 | $[In_{10}O_{15}..H_2O]^A \rightarrow In_{10}O_{16} + H_2$ | 2.9 | 4.35 | 1.45 |
| 3 | $H_2O \rightarrow _{1/2}O_2+H_2$ | 2.83 | 2.94 | 0.10 |

## 4. Conclusions

Density Functional Theory and transition state method calculations were employed to examine the theoretical values of the interaction between indium oxide and water molecules. A clear increase in the energy gap value of Indium Oxide is observed when interacting with water; as a result, the resistance is found to increase, and the conductivity is found to decrease. However, the increased oxygen atoms within increased Gibbs free energy are suggested to indicate that the reaction is considered to be endergonic. The reaction product is $In_{10}O_{16}$, and the release of hydrogen gas was found to occur through a photocatalysis process.

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## References

[1] Jia, T. Q.; Sun, H. Y.; Li, X. X.; Feng, D. H.; Li, C. B.; Xu, S. Z.; and Sun, Z. R.; et. al.; “The Ultrafast Excitation Processes in Femtosecond Laser-Induced Damage in Dielectric Omnidirectional Reflectors”. J. Appl. Phys. 100(2): 023103, 2006.

[2] Si, M.; Lin, Z.; Charnas, A.; and Ye, P.D.; "Scaled Atomic-Layer-Deposited Indium Oxide Nanometer Transistors With Maximum Drain Current Exceeding 2 A/mm at Drain Voltage of 0.7 V". IEEE Electron Device Lett.*,* 42(2): 184-187, 2021.

[3] Sharma, N.; Sharma, B.; Das, S. K.; Chettri, P.; Karki, P.; Pradhan, R.; and Pradhan, A.; et. al.; “A First-Principle Study to Investigate Electrical and Optical Properties of Tin Oxide”. Proc. 2024 IEEE Int. Conf. Electron Devices Society Kolkata Chapter (EDKCON), Kolkata, India, 30 November; IEEE Conf. Series: New Jersey, United States, 2024.

[4] Swallow, J.E.N.; Palgrave, R.G.; Murgatroyd, P.A.E.; Regoutz, A.; Lorenz, M.; Hassa, A.; and Grundmann, M.; *et al.*; "Indium Gallium Oxide Alloys: Electronic Structure, Optical Gap, Surface Space Charge, and Chemical Trends within Common-Cation Semiconductors". ACS Appl. Mater. Interfaces*,* 13(2): 2807-2819, 2021.

[5] Kumar, V.; Chauhan, V.; Ram, J.; Gupta, R.; Kumar, S.; Chaudhary, P.; and Yadav, B. C.; *et al.*; "Study of humidity sensing properties and ion beam induced modifications in $SnO_2$-$TiO_2$ nanocomposite thin films". Surf. Coat. Technol.*,* 392(6): 125768, 2020.

[6] Li, C.; Choi, P.G.; and Masuda, Y.; "Large-lateral-area $SnO_2$ nanosheets with a loose structure for high-performance acetone sensor at the ppt level". J. Hazard. Mater.*,* 455(8): 131592, 2023.

[7] Xu, C.; Tamaki, J.; Miura, N.; Yamazoe, N.; "Grain size effects on gas sensitivity of porous $SnO_2$-based elements". Sens. Actuators B Chem.*,* 3(2): 147-155, 1991.

[8] Liang, Y.X.; Chen, Y.J.; Wang, T.H.; "Low-resistance gas sensors fabricated from multiwalled carbon nanotubes coated with a thin tin oxide layer". Appl. Phys. Lett.*,* 85(4): 666-668, 2004.

[9] Chiorino, A.; Ghiotti, G.; Prinetto, F.; Carotta, M.C.; Malagù, C.; Martinelli, G.; "Preparation and characterization of $SnO_2$ and $WO_x$–$SnO_2$ nanosized powders and thick films for gas sensing". Sens. Actuators B Chem.*,* 78(1): 89-97, 2001.

[10] Li, P.; Fan, H.; Cai, Y.; "$In_2O_3$/$SnO_2$ heterojunction microstructures: Facile room temperature solid-state synthesis and enhanced $Cl_2$ sensing performance". Sens. Actuators B Chem.*,* 185(8): 110-116, 2013.

[11] Lu, G.; Ocola, L.E.; Chen, J.; "Room-Temperature Gas Sensing Based on Electron Transfer between Discrete Tin Oxide Nanocrystals and Multiwalled Carbon Nanotubes". Adv. Mater.*,* 21(24): 2487-2491, 2009.

[12] Sharma, A.; Tomar, M.; Gupta, V.; "Room temperature trace level detection of $NO_2$ gas using $SnO_2$ modified carbon nanotubes based sensor". J. Mater. Chem.*,* 22(44): 23608-23616, 2012.

[13] Bahuguna, G.; Mondal, I.; Verma, M.; Kumar, M.; Bhattacharya, S.; Gupta, R.; and Rathi, A.; et. al.; “Innovative Approach to Photo-Chemiresistive Sensing Technology: Surface-Fluorinated $SnO_2$ for VOC Detection”. ACS Appl. Mater. Interfaces 12(33): 37320–37329, 2020.

[14] Jafer, N. F.; and Hussein, M.; “Study of the Transition State of $SnO_2$ Cluster with $NO_2$ Gas Molecule via Density Functional Theory”. Int. J. Nanosci. 21(01): 2250006, 2022.

[15] Abdulradha, S. K.; Hussein, M.; and Abdulsattar, M. A.; “Study of the Interaction Between Reduced Graphene Oxide and $NO_2$ Gas Molecules via Density Functional Theory (DFT)”. Int. J. Nanosci. 21(02): 2250009, 2022.

[16] Abdulridha, S.K.; Abdulsattar, M.A.; Hussein, M.T.; "Sensitivity of $SnO_2$ nanoparticles/reduced graphene oxide hybrid to $NO_2$ gas: a DFT study". Struct. Chem.*,* 33(6): 2033-2041, 2022.

[17] Hussein, M.; Fayad, T.; Abdulsattar, M.; "Concentration effects on electronic and spectroscopic properties of ZnCdS wurtzoids: a

density functional theory study". Chalcogenide Lett., 16(11): 557-563, 2019.

[18] Hussein, M.T.; Thjeel, H.A.; "Vibration Properties of ZnS nanostructure Wurtzoids: ADFT Study". In: Proceedings of the International Workshop in Physics Applications, Fallujah, Anbar, Iraq, 20–21 November; IOP Publishing: England, United Kingdom, 2019.

[19] Abdulsattar, M.A.; "Transition state theory application to $H_2$ gas sensitivity of pristine and Pd doped $SnO_2$ clusters". Karbala Int. J. Mod. Sci., 6(2): 13-20, 2020.

[20] Abdulsattar, M.; Hussein, M.; Kahaly, M.; "Effect of reduced graphene oxide hybridization on ZnO nanoparticles sensitivity to $NO_2$ gas: A DFT study". J. Ovonic Res., 19(2): 153-163, 2023.

[21] Louie, S.G. "Chapter 2: Predicting Materials and Properties: Theory of the Ground and Excited State." In Contemporary Concepts of Condensed Matter Science, Vol. 2; Louie, S.G., and Cohen, M.L., Eds.; Elsevier: Amsterdam, Netherlands, pp. 9–53, 2006.

[22] Zhang, H.; Yang, J.; "First-principles study on the structural and electronic properties of $In_2O_3$ nanoclusters". J. Phys. Chem. C, 115(16): 7721–7726, 2011.

[23 ] Li, C.; Zhang, D.; Liu, X.; Han, S.; Tang, T.; Han, J.; and Zhou, C.; "$In_2O_3$ Nanowires as Chemical Sensors." Appl. Phys. Lett., 82(10): 1613–1615, 2003.

[24] Kuang, P.; Park, J.-M.; Leung, W.; Mahadevapuram, R.C.; Nalwa, K.S.; Kim, T.-G.; and Chaudhary, S.; et al.; "A New Architecture for Transparent Electrodes: Relieving the Trade-Off Between Electrical Conductivity and Optical Transmittance." Adv. Mater., 23(21): 2469–2473, 2011.

[25] Xiao, F.; He, Z.; Zheng, Y.; Xiong, S.; and Cheng, Q.; "A DFT Study on Mechanisms of Indium Adsorption on Sphalerite (100), (110), and (111) Surfaces: Implications for Critical Metal Mineralization." Ore Geol. Rev., 181(6): 106572, 2025.

[26] Azeez, Y.H., Kareem, R.O., Qader, A.F., Omer, R.A., and Ahmed, L.O. "Spectroscopic characteristics, stability, reactivity, and corrosion inhibition of AHPE-dop compounds incorporating (B, Fe, Ga, Ti): A DFT investigation", Next. Mater., 3(4): 100184, 2024.

[27] Inerbaev, T.; Sahara, R.; Mizuseki, H.; Kawazoe, Y.; and Nakamura, T. "Theoretical Modeling of Oxygen and Water Adsorption on Indium Oxide (111) Surface." In Photoinduced Processes at Surfaces and in Nanomaterials, Vol. 1196; American Chemical Society: Washington, D.C., United States, pp. 137–149, 2015.

[28] Temkin, O.N.; "'Golden Age' of Homogeneous Catalytic Chemistry of Alkynes: Some Oxidative Transformations of Alkynes (A Review)." Kinet. Catal., 64(5): 521–577, 2023.

[30] Zhang, B.; Zhang, N.N.; Chen, J.F.; Hou, Y.; Yang, S.; Guo, J.W.; et al.; "Turning Indium Oxide into a Superior Electrocatalyst: Deterministic Heteroatoms." Sci. Rep., 3(1): 3109, 2013.

[31] Zhanpeisov, N.U.; Nakatani, H.; Fukumura, H.; "Theoretical DFT study of the structure and chemical activity of small indium(III) oxide clusters". Res. Chem. Intermed., 37(6): 647-658, 2011.

[32] Chen, H.; Blatnik, M.A.; Ritterhoff, C.L.; Sokolović, I.; Mirabella, F.; Franceschi, G.; et al.; "Water Structures Reveal Local Hydrophobicity on the $In_2O_3$(111) Surface." ACS Nano, 16(12): 21163–21173, 2022.

[33] Hassan, S.F. and El-Shahawy, A.S.; "Preparation and study of indium oxide nanoparticles using DFT method." Int. J. Nanosci. Nanotechnol., 11(3): 203–210, 2022.

[34] Jiang, X.; Nie, X.; Gong, Y.; Moran, C.M.; Wang, J.; Zhu, J.; and Zhang, H. et al.; "A combined experimental and DFT study of $H_2O$ effect on $In_2O_3/ZrO_2$ catalyst for $CO_2$ hydrogenation to methanol." J. Catal., 383: 283–296, 2020.

[35] Chen, H.; Blatnik, M.A.; Ritterhoff, C.L.; Sokolović, I.; Mirabella, F.; Franceschi, G.; and Müller, T. et al.; "Water Structures Reveal Local Hydrophobicity on the $In_2O_3$(111) Surface." ACS Nano, 16(12): 21163–21173, 2022.

[36] Perera, D.C. and Rasaiah, J.C.; "Exchange Functionals and Basis Sets for Density Functional Theory Studies of Water Splitting on Selected ZnO Nanocluster Catalysts." ACS Omega, 7(15): 12556–12569, 2022.

[37] Perera, D.C. and Rasaiah, J.C.; "Computational Study of $H_2O$ Adsorption, Hydrolysis, and Water Splitting on $(ZnO)_3$ Nanoclusters Deposited on Graphene and Graphene Oxides." ACS Omega, 8(35): 32185–32203, 2023.