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Study of the electronic properties of pure nanostructured hexagonal Zinc Oxide by DFT method

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Abstract:

(ZnO) Zinc oxide is considered a semiconducting material from the family of transparent conductive oxide materials. Our study aims to study the electronic properties of pure Nano-sized hexagonal zinc oxide using the DFT method using the (GGA-PBE) approximation and the (HSE03) approximation, as we demonstrated through our study on the unit cell In the large cell (3×3×3) and the small cell (1×1×1), zinc oxide has a direct energy gap in the (GGA-PBE) approximation, and its value is (e V) 1.74) and in the (HSE03) approximation, the value of the energy gap is (e V2.79). The difference in the two approximations is very clear, and it is evidence that when using the (GGA-PBE) approximation for the DFT method, it reduces the value of the energy gap for zinc oxide, and when using the (HSE03) approximation, the energy gap increases because it is more mathematically accurate, even though it takes more time to calculate.

Keywords: h-ZnO, density function theory (DFT), approximation (GGA-PBE), CASTEP program, electronic properties of pure hexagonal Zinc Oxide, hybrid approximation (HSE03).

دراسة الخواص الإلكترونية لأوكسيد الزنك السداسي النقي النانوي بطريقة *DFT*

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الخلاصة:

(*Zn O*) أوكسيد الزنك يعتبر مادة شبه موصلة من عائلة مواد الأكاسيد الشفافة الموصلة .الهدف من دراستنا هو دراسة الخواص الإلكترونية لأوكسيد الزنك السداسي النقي النانوي بطريقة *DFT* باستخدام تقريب(*GGA-PBE*) وتقريب (*HSE03*) ،حيث أثبتنا من خلال دراستنا على وحدة الخلية الكبيرة(٣×٣×٣) والخلية الصغيرة (١×١×١)، إن أوكسيد الزنك يملك فجوة طاقة مباشرة في تقريب(*GGA-PBE*) وتبلغ قيمته *1.74 (e V)* وفي تقريب (*HSE03*) يبلغ قيمة فجوة الطاقة (*e V2.79*). إن الفرق في التقريبين واضح جدا وهو دليل على أنه عند استخدام تقريب(*GGA-PBE*) لطريقة *DFT* فانة يقلل من قيمة فجوة الطاقة لأوكسيد الزنك وعند استخدام تقريب (*HSE03*) تزداد فجوة الطاقة لكونها أكثر دقة حسابيا رغم أنها تستغرق وقت أكثر في الحساب .

الكلمات المفتاحية: h-ZnO، نظرية الكثافة الدالية (DFT)، التقريب (GGA-PBE)، برنامج CASTEP، الخواص الإلكترونية لأكسيد الزنك السداسي النقي، تقريب (HSE03) الهجين.

1. INTRODUCTION:

Since graphene appeared in the headlines and was rediscovered in 2004-2005, there has been and continues to be an increase in interest in isolating and using other new two-dimensional materials. Two-dimensional materials such as hexagonal zinc oxide (h-ZnO) and graphene possess a set of properties that are used in a large number of scientific disciplines and on a wide industrial scale for manufacturing across many fields in the search for significantly improved device performance, starting with sensing **[1]**. Through energy storage and generation and carbon-based molecular electronics **[2] [3]**semiconductors with hexagonal transition elements **[4-12]** (II-VI) in the periodic table crystallize in a hexagonal close-packed (HC) system and can Zinc oxide (ZnO) exists in nature in the form of a powder or solid crystal **[13]** and depending on the conditions of preparation. It features a wide direct n-type bandgap at 300K°. The benefit of the large bandgap is to withstand large electric fields with the added benefit of low electrical noise. The strong correlation energy (60mev) is also distinguished by the fact that it can be used to make an energy-based laser **[6 ,14]** with wonderful physical properties, which makes it one of the most widely used materials in various fields such as photoelectrons and photovoltaic cells. Researchers have been interested in Zinc oxide is currently used for its uses in various electronic **[15]**, industrial, military, medical, chemical, physical, biomedical, and other fields.

Hexagonal zinc oxide is characterized by high electron mobility, a non-toxic nature, and excellent photocatalytic activity by ultraviolet radiation. (Zn-O) leads to the fact that (sp^2) hybridization in the two-dimensional graphene-like honeycomb structure is stronger than (sp^3) hybridization in bulk zinc oxide crystals. In addition, hexagonal zinc oxide is highly resistant to strong radiation and shows remarkable photoluminescence **[16 ,17]**.

2. Method for calculating electronic properties:

The electronic properties of pure hexagonal zinc oxide were studied using First Principle Calculations **[18]** using Density Functional Theory (DFT), Generalized Gradient Approximation (GGA), and using the Perdew – Burke approximation. Ernzerhof (PBE) for the possibility of exchange correlation energy and also used the hybrid HSE03 approximation **[19, 20]** hybrid functional based on a screened Coulomb potential to be more mathematically accurate for the energy gap in the program **[21]** (CASTAP) and it was used to describe the electronic valence structure of Zinc Oxide Pure hexagon($Zn - 3d^{10}\,4S^2$, $O - \ 2S^2\ 2P^4$).

3. Results and Calculations:

3.1. Bond length of pure nanoparticle hexagonal zinc oxide:

The calculations were carried out on the small unit cell (1×1×1), the large unit cell (3×3×3), (3×3×1), and the large unit cell (4×4×1), and it gives the same results whether the large cell is taken or not. The small cell was taken (1×1×1). Zinc oxide consists of 8 atoms of oxygen and 30 atoms of zinc, which are the lattice parameters (a, b, c). (a=b= 3.525 Aº) in the plane (X, Y). As for the value of (c), which represents the distance between each two layers, it was chosen (c=5.025 Aº) (in the direction of the Z axis).) This large distance was chosen for calculation purposes as it is possible in this case, the interaction between the layers is neglected, so that the calculated properties of zinc oxide with one layer (layer) only and not the bulk (bulk), the length of the bond according to practical measurements, the original length of the bond is (1.501 Aº) and after the Geometry Optimization procedure it became (1.976 Aº) as shown in **Figure (1-a)**. The primitive cell unit consists of the original lattice constants (a=b=2.600, c=30.00 Aº). The first Berlion region is set at point k. (11×11×2) as for the angle between the atoms bonded to each other for zinc and oxygen (Zn-O-Zn)، it is equal to (120°) as shown in **Figure (1-b)**. Also, the lattice parameters (a, b, c). (a=b= 3.525 Aº) in the plane, only one, as in this case the interaction between the classes can be neglected.

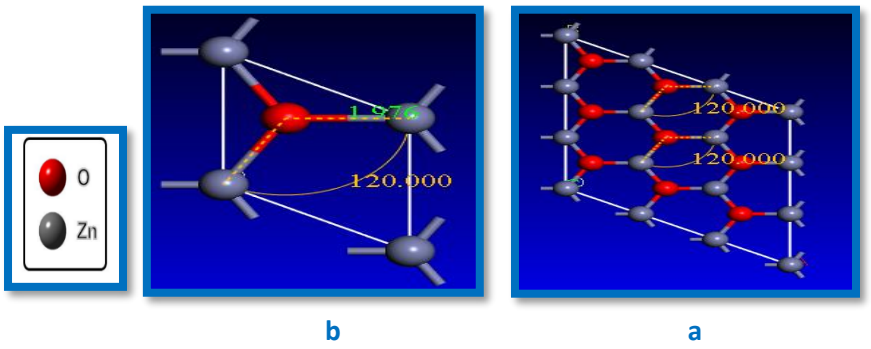

Figure 1: Hexagonal Pure Zinc Oxide cell after Conditioning and the Value of the angle between (Zn-O-Zn).

3.2. Electronic properties of hexagonal zinc oxide sheets:

3.2.1. Calculate energy packets using the (GGA-PBE) approximation:

The band gap is defined as the energy required to excite (transfer) electrons from the top of the valence band to the conduction band. It is called forbidden because it is a place free of electronic states and in which electrons do not settle in pure semiconductors. The energy gap allows one to distinguish between insulators. Semiconductors, metals, and conductors. The value of the energy gap for pure hexagonal zinc oxide is calculated through the values of the difference between the two closest points in the conduction band and the valence band, and determining whether the gap is direct or indirect .I calculated the electronic properties of zinc oxide, including the band structures, and determined the samples of the first Berlion region at the k point (11×11×2) of the lattice using (GGA-PBE) calculations for a pure hexagonal zinc oxide sheet. From the results, we notice an energy gap of 1.742 eV directly at Point (K) as shown in **Figure (2)**. It is known that the (GGA-PBE) approximation using DFT theory generally underestimates the band gap in pure hexagonal zinc oxide, and the reduction of the energy gap occurs in the (GGA) approximation in ZnO, so we used (HSE03) approximates the hybrid, which will be explained later in detail.

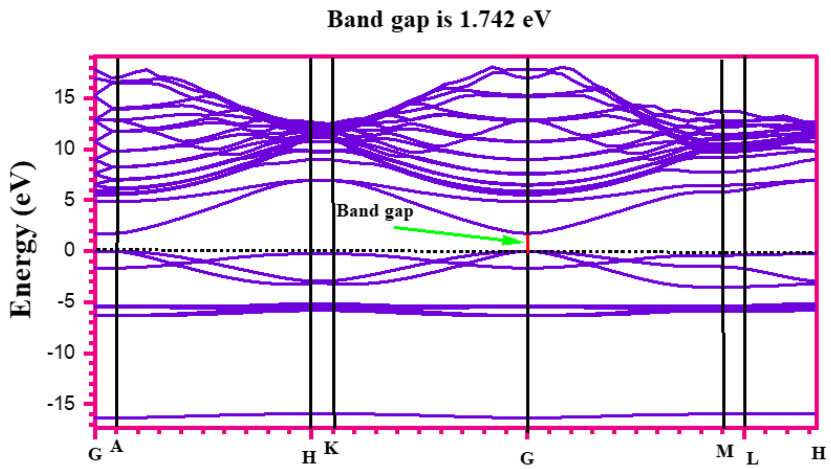

Figure (2) Structures of the electronic states (band gap) of pure hexagonal zinc oxide sheet using the (GGA-PBE) approximation.

3.2.2. Calculate energy packages using approximation (HSE03)

The hybrid (HSE03) approximation can describe the electron self-interaction better than the (GGA-PBE) approximation، and the calculation results are closer to the experimental values, although it is time and computationally expensive. **Figure (3)** shows the beam structures using the (HSE03) approximation. The points were taken at the K point (4×4×1) using the (HSE03) approximation for a pure hexagonal zinc oxide plate on the small cell (1×1×1) because it gives the same results as the large cell calculations. To calculate the band gap، we take the difference between the two closest points in the conduction and valence bands. We notice when performing the calculations that the energy gap is (2.794 eV) at point (K)، which is a direct energy gap، meaning that the energy gap has changed and become wider than it was when it was calculated. In the (GGA-PBE) approximation (GGA-PBE) and an approximation to the results of experimental calculations **[22, 23]**, these types of the broad bandgap of (2D ZnO) have the potential to be implemented in nanoscale UV-optoelectronics via nonstructural engineering. The direct and indirect band gap can be compared. If the band gap is direct, the electron releases its energy in the form of a photon. If the band gap is indirect, it releases its energy in the form of a phonon. The transfer of electrons between the conduction and valence bands is useful in several applications, the most important of which are solar cell, lasers, masers, and light diodes. **Table (1)** shows a comparison between the current study and previous studies of 2D hexagonal ZnO for the lattice, energy gap, approximation, and device used.

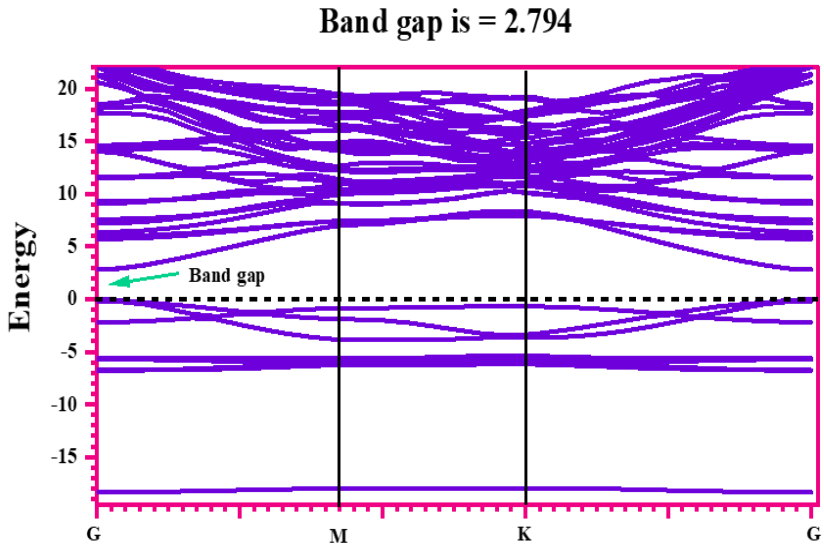

Figure (3) shows the structures of the electronic states (band gap) of a pure hexagonal zinc oxide sheet using the (HSE03) approximation.

Table (1) shows a comparison between the current study and previous studies of two-dimensional hexagonal zinc oxide for the lattice, energy gap, approximation, and device used.

Material	Structure	Bandgap (eV)	XC functional	Program	Ref
	Hexagonal	4.48 eV 4.20 eV	HSE03	DFT	[22 ,23]
2D-Zn O	Hexagonal	1.75 e V	PW91 sRef. 26d	CASTAP	[24]
	Hexagonal	1.68eV	GGA	DFT	[25]
	Hexagonal	1.742 eV	GGA-PBE	CASTAP	in this study
	Hexagonal	2. 794 eV	HSE03	CASTAP	in this study

4. Total density of states (TDOS)

4.1. Total density of states using the GGA-PBE approximation

Density of states in materials physics. The condensed state describes the proportion of states that the system must occupy at each energy. The total density of states is obtained by summing the peaks of all the bands. I calculated the density of states. I took the density of states at the point k (1 x 1 x 1) using (GGA- PBE) **Figure (4)** represents the energy changes in terms of energy, where we notice the density of states in the extended field (0-18.6 (eV)) representing the conduction band, and this means that there is a critical temperature at which the density of states is high and a noticeable change appears at (3.5 e\eV). This was done. A high density of states was also recorded in the extended field.

((-16.6) - 0 (eV)) which represents the valence band region and the presence of the first peak in the extended field ((-16.8)-(-15.3 e\ eV)) which is estimated at (3.4 e \eV) after which the density of states disappears. The second peak in the extended field ((-6.87)-(-4.63eV)), which is estimated at ((11.6(e\eV)) and then disappears, the density of states is high for zinc for the 2p orbital) in the beam The valence band is rich in electrons with the ability to move, and at this energy, the ability to move the electrons is for the conduction band. It can be noted that the valence band near the Fermi level is dominated by O-2p with a small contribution from the Zn-3d states, and the conduction band mainly contributed to the states (O-2p, Zn-4s). The third peak in the valence band is in the extended field ((-3.94)-0.06(e\ eV)) the density is estimated at (2.87 e\ eV) in the valence band region. The density of electronic states is symmetric for both spin and spin. The symmetrical electron density causes the magnetic moment of this material to be zero, which indicates that zinc oxide is a non-magnetic semiconductor material.

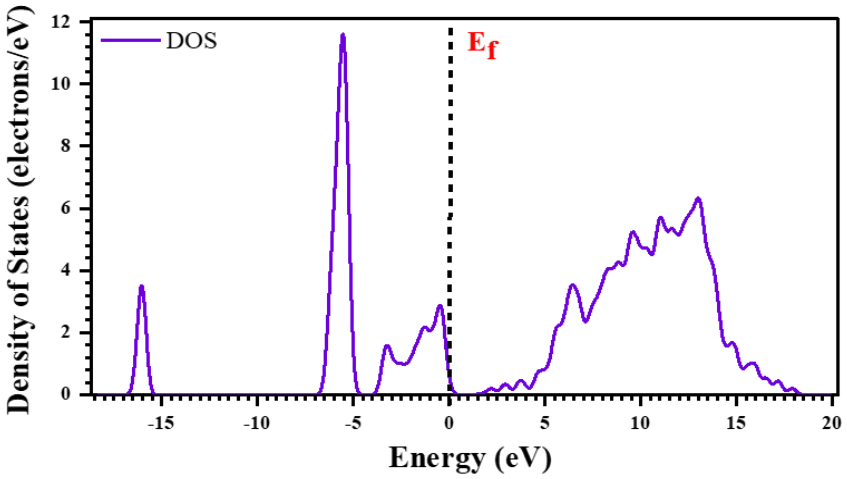

Figure (4) shows the electronic state structures (total density) of pure hexagonal zinc oxide sheets using the (GGA-PBE) approximation.

4.2. Total density of states using the approximation (HSE03)

To know the extent of the effect of the hybrid (HSE03) approximation on the overall density of states of the GGA-PBE approximation, we note that the energy field extending from (0- 21 (e V)) In **Figure (5)** is called the conduction band. We notice a noticeable change from (0.5-18 (e V)) where the density of states varies because of the high temperatures in these areas of energy. The highest density of states is recorded in the conduction region at energy (10.1 eV) and reaches (5.1). The valence band is the energy field extending from (0-(-20) e V). We notice a first peak extending from ((-20.1)-(-22.8) (e V)) after which there is no density. The states are a result of the possibility of the electrons not being transferred. We notice in the energy range from ((-17.1)-0.67(e V)) the occurrence of different density states in the energy values and peaks, which means that they are rich in electrons that can move freely between energy levels. We note that the regions near The Fermi level are where the density of states for the conduction and valence bands decreases due to the lack of electrons in them. It becomes clear to us from the density of states in the regions of the conduction band and the valence band that the regions in which electrons are present, i.e., rich in electrons, have peaks of state density in which there are no electrons, i.e., poor in electrons. We notice that there is not a significant difference in the overall density of states for both the (GGA) approximations and the hybrid (HSE03) approximation.

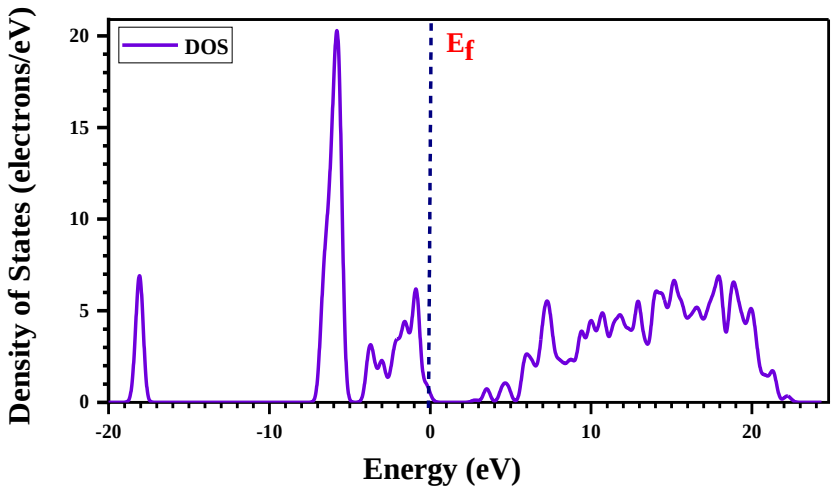

Figure (5) shows a pure hexagonal zinc oxide sheet's electronic state structures (total density) using the HSE03 approximation.

5. Conclusions

The purpose of the research is to study the electronic properties of pure Nano-hexagonal zinc oxide using the DFT method. We found that when calculating the electronic structures (densities of total and partial states) using the generalized gradient approximation (GGA), where the density of states in the extended field (0-18.6 (eV)) this region represents the conduction band This means that there is a high temperature, meaning there are many conductive electrons, the density of states is high, and a noticeable change appears at (3.5 e\eV). This is due to the lack of transfer of electrons that cannot break the Coulomb potential barrier. We found that if we modify and prepare the geometry of the zinc oxide network, the length of the bond increases from the original length (1.501 A ˚ - 1.97 A ˚) and that the resulting increase does not affect the structure of the network. When calculating the beam structures using the generalized gradient approximation (GGA-PBE), we found that it is equal to (1.74e V), and it turns out that the energy beams fall on the same values of (K) at the first Brillion point, meaning that the energy gap is direct band gap. When calculating the beam structures, we found that the energy gap using the hybrid (HSE03) approximation, which is equal to (2.79 e V) at point (K), is that the energy gap is direct. We found out through our theoretical calculations in the CASTAP program and using DFT theory that the energy gap lies at the same values as (K), which is a direct band gap using the two approximations, the (GGA-PBE) approximation and the (HSE03) hybrid approximation. Now the hybrid approximation does not reduce the value of the band. The range of pure hexagonal zinc oxide nanoparticles, in contrast to the (GGA-PBE) approximation, shows us that hexagonal zinc oxide has a wide bandgap. It is a semiconductor material and is used in electronics applications and energy electron emitters.

6 .References:

[1] Slate AJ, Karaky N, Whitehead KA. Antimicrobial properties of modified graphene and other advanced 2D material coated surfaces. 2018.

[2] Novoselov KS, Geim AK, Morozov SV, Jiang D-e, Zhang Y, Dubonos SV, et al. Electric field effect in atomically thin carbon films. science. 2004;306(5696):666-9.

[3] Chung K, Lee C-H, Yi G-C. Transferable GaN layers grown on ZnO-coated graphene layers for optoelectronic devices. Science. 2010;330(6004):655-7.

[4] Janotti A, Van de Walle CG. Fundamentals of zinc oxide as a semiconductor. Reports on progress in physics. 2009;72(12):126501.

[5] Pearton S, Norton D, Ip K, Heo Y, Steiner T. RETRACTED: Recent progress in processing and properties of ZnO. Progress in materials science. 2005;50(3):293-340.

[6] Özgür Ü, Alivov YI, Liu C, Teke A, Reshchikov MA, Doğan S, et al. A comprehensive review of ZnO materials and devices. Journal of Applied Physics. 2005;98(4).

[7] Tsukazaki A, Ohtomo A, Onuma T, Ohtani M, Makino T, Sumiya M, et al. Repeated temperature modulation epitaxy for p-type doping and light-emitting diode based on ZnO. Nature materials. 2005;4(1):42-6.

[8] Repins I, Contreras MA, Egaas B, DeHart C, Scharf J, Perkins CL, et al. 19· 9%-efficient ZnO/CdS/CuInGaSe2 solar cell with 81· 2% fill factor. Progress in Photovoltaics: Research and applications. 2008;16(3):235-9.

[9] Morkoç H, Özgür Ü. Zinc oxide: fundamentals, materials and device technology: John Wiley & Sons; 2008.

[10] Klingshirn C. ZnO: From basics towards applications. physica status solidi (b). 2007;244(9):3027-73.

[11] Guo H, Lu N, Dai J, Zeng XC, Wu X, Yang J. Electronic structure engineering in chemically modified ultrathin ZnO nanofilms via a built-in heterointerface. RSC Advances. 2014;4(36):18718-23.

[12] Behera H, Mukhopadhyay G. Strain-tunable band parameters of ZnO monolayer in graphene-like honeycomb structure. Physics Letters A. 2012;376(45):3287-9.

[13] Rahal A. Elaboration des verres conducteurs par déposition de ZnO sur des verres ordinaires. UNIVERSITE D'ELOUED. 2013.

[14] Topsakal M, Cahangirov S, Bekaroglu E, Ciraci S. A First-Principles Study of Zinc Oxide Honeycomb Structures. Bulletin of the American Physical Society. 2010;55.

[15] Pan Q, Liu BH, McBriarty M, Martynova Y, Groot I, Wang S, et al. Reactivity of ultra-thin ZnO films supported by Ag (111) and Cu (111): a comparison to ZnO/Pt (111). Catalysis letters. 2014;144:648-55.

[16] Freeman CL, Claeyssens F, Allan NL, Harding JH. Graphitic nanofilms as precursors to wurtzite films: theory. Physical review letters. 2006;96(6):066102.

[17] Tusche C, Meyerheim H, Kirschner J. Observation of depolarized ZnO (0001) monolayers: formation of unreconstructed planar sheets. Physical review letters. 2007;99(2):026102.

[18] Freysoldt C, Grabowski B, Hickel T, Neugebauer J, Kresse G, Janotti A, et al. First-principles calculations for point defects in solids. Reviews of modern physics. 2014;86(1):253.

[19] Niraula PR. Density functional theory study of two-dimensional boron nitride films: City University of New York; 2020.

[20] Chakarawet K, Debus RJ, Britt RD. Mutation of a metal ligand stabilizes the high-spin form of the S2 state in the O2-producing Mn4CaO5 cluster of photosystem II. Photosynthesis Research. 2023:1-6.

[21] Rutter MJ. C2x: A tool for visualisation and input preparation for Castep and other electronic structure codes. Computer Physics Communications. 2018;225:174-9.

[22] Lee J, Sorescu DC, Deng X. Tunable lattice constant and band gap of single-and few-layer ZnO. The journal of physical chemistry letters. 2016;7(7):1335-40.

[23] Supatutkul C, Pramchu S, Jaroenjittichai A, Laosiritaworn Y, editors. Electronic properties of two-dimensional zinc oxide in hexagonal,(4, 4)-tetragonal, and (4, 8)-tetragonal structures by using Hybrid Functional calculation. Journal of Physics: Conference Series; 2017: IOP Publishing.

[24] Ma X, Wu Y, Lv Y, Zhu Y. Correlation effects on lattice relaxation and electronic structure of ZnO within the GGA+ U formalism. The Journal of Physical Chemistry C. 2013;117(49):26029-39.

[25] Tu Z. First-principles study on physical properties of a single ZnO monolayer with graphene-like structure. Journal of Computational and Theoretical Nanoscience. 2010;7(6):1182-6.