INTERNATIONAL CONFERENCE ON
SCIENCE AND ENGINEERING
1st December 2015 DUBAI - UAE
کنفرانس بین المللی علوم و مهندسی
۱۰ آذرماه ۱۳۹۴ دبی - امارات

Structural and electronic properties of zinc oxide nanostructures via density functional theory

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Abstract
By using ab initio density functional theory we studied the structural and electronic properties of zinc oxide, monolayer, double layer graphenlike and nanoribbons with armchair and zigzag edges. In case the double layer, the effects of inter-layer coupling on the electronic structures, were observed. These results showed that the energy gap in the monolayer was closed by inter-layer coupling. It was found that the ZnO double layer has a metallic behavior. Our results showed zigzag ZnO nanoribbons have metalic property, but ZnO armchair nanoribbons showed semiconductor behavior.

Keywords: ZnO nanostructures, electronic structure, DFT.

Introduction

From ۱۹۹۱ that Iijima [۱] discovered carbon nanotubes, it has done a vast studies of different variety of organic and nonorganic nanostructures [۲]. Bulk Zinc oxide has direct band gap of ۳,٤ eV and an excitonic energy of ٦۰ m eV at room temperature. Therefor it is a promising material for high-effeciency blue and ultraviolet optical devices. Zinc oxide with a direct band gap has vast applications on optoelectronics, spintronics and transducers [۳, ٤]. Already ZnO different morphologies have been fabricated [٤, ٥]. Also graphenlike hexagonal zinc oxide nanostructures have been fabricated [٦], because of possible potential applications [۷, ۸, ۹, ۱۰]. Both experimental and theoretical studies showed that zinc oxide nanostructures have unique electronic, magnetic and optic properties. For example many devices are fabricated by one dimensional zinc oxide, similar nanolasers, and UV detectors [۱۱]. This, have been showed that ZnO nanostructures are important materials in order to fabricate of nanodevices in future.

Computational details and results

Crystalline ZnO single layer, double layer, armchair and zigzag nanoribbons, could be modeled using a supercell. Total energy, density of states, band structures and electronic densities are calculated via first principles full potential linearized augmented plane wave (LAPW) density functional theory as implemented in the WIEN۲K code [۱۲]. For the exchange and correlation energies, the generalized gradient approximation (GGA) is used [۱۳]. The Zn ۳d electrons were treated as part of the valance band. The total number of k-point in the whole Brillouin zone is taken to be ۲۰۰. The value of the $R_{mt}K_{max}$ is taken to be ۷. $R_{mt}K_{max}$ in the WIEN۲K package is a parameter such that appropriate choice of it determines the convergence of the calculations. This value controls the size of the basis sets in the calculations.

۱- ZnO graphenlike single layer (SL)

First total energy, density of state and band structure of a ZnO hexagonal single layer was calculated. In order to perform calculations the values of the Zn-O bound is taken to be ۱،۸۵۳ Å [۲]. Unit cell containing ۲ Zn and ۲ O atoms is shown in Figure ۱(a).The bigger sphere shows the zinc atom and the smaller one is oxygen atom. Fig. ۱(b) shows a ZnO graphenlike single layer. Density of states, (DOS) and band structure, (BS) for this monolayer are showed in figure ۲. It is seen that this structure is a semiconductor with a direct energy gap of ۱،۹۰ eV in Γ point BZ. It is seen a sharp peak in density of states, that it shows ۳d level electrons in Zn atom.

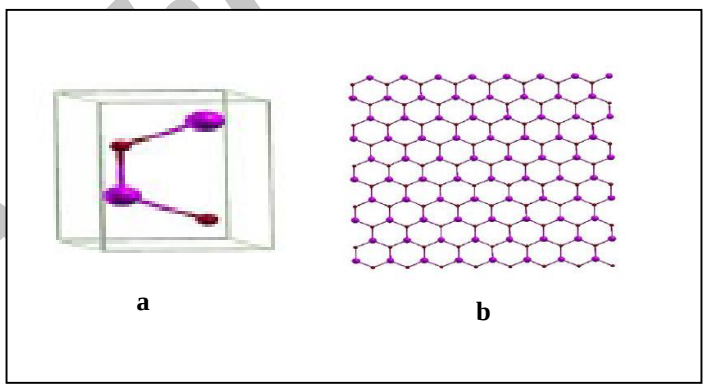


Fig.۱, (a): A supercell of ZnO graphenlike single layer
(b): and a single layer of them (b).

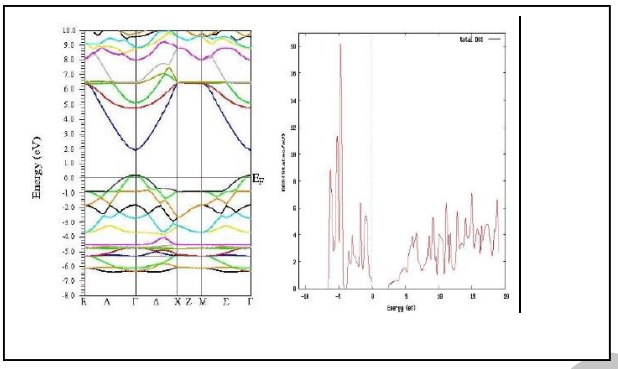


Fig.۲: DOS and BS of ZnO graphenlike single layer.

۲- ZnO simple graphenlike double layer, (SDL)

We considered a system of ZnO double layers such that the Zn atoms in the first layer are just above of Zn atoms in the second layer, named simple double layer, (SDL). Fig. ۳(a) shows this structure, and in the Fig. ۳(b), Fig. ٤, the total energy, DOS, BS and electronic density, (ED), of the SDL are respectively seen. It's seen the minimum total energy was happen when the interval of the two layers is ٤,۱۲ Å.

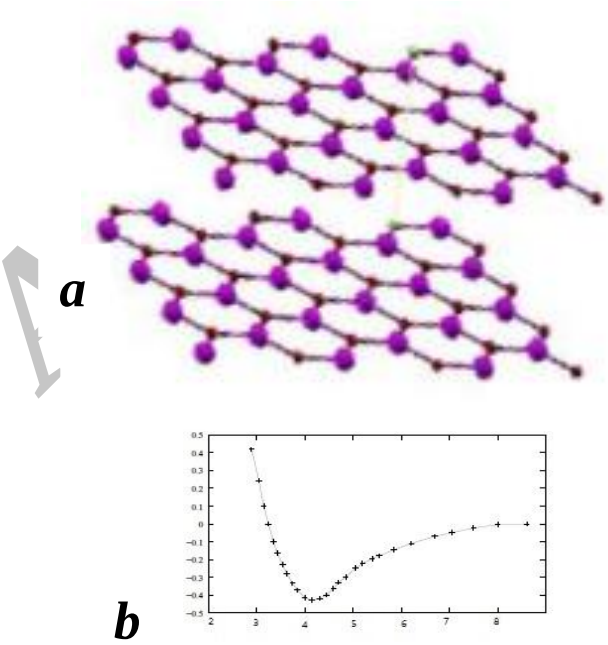


Fig.۳:a) ZnO simple graphenlike double layer, (SDL), b) Total energy of simple graphenlike double layer, (SDL) vs. interlayer distance.

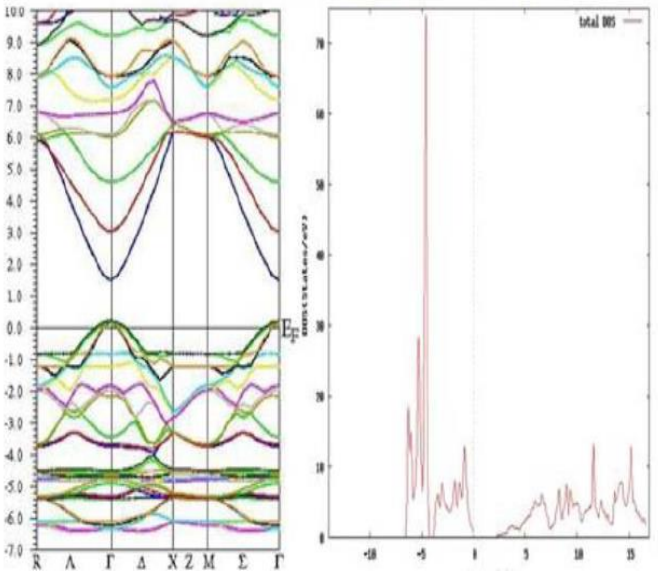
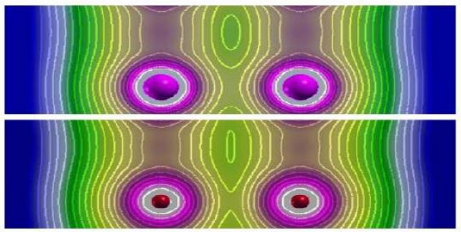


Fig. ٤: Band structure and density of states of SDL.



Colure	ED
Blue	٠,٠٠٠٥
indigo	٠,٠٠٣٢
Green	٠,٠١٩٩
Yellow	٠,١٢٥٦
Violet	o.٧٩٢٤
White	٥,٠٠٠٠

Fig.٥: Electronic density of SDL, (ED).

From Fig.٤ it's seen that SDL has a ١,٦٠ eV band gap. This is direct band gap in Γ point BZ. Fig. ٥ shows the condensation of yellow colure among of the Zn atoms, showing electronic density in this region. As it is seen from the figure, white, violet, yellow, green, indigo and blue colures have the most electronic densities respectively. To draw of Fig. ٣(b) and the other similar curves we have used the relation (١), where E_{tot} , N_{tot} is total energy of the system, E_{Zn} , N_{Zn} , E_O , N_O, and E_{bin} are total energy of the system, total number of the atoms, energy of Zn atom, the number of Zn atoms, energy of O atom, number of O atoms in a supercell and binding energy of the system respectively.

$$E_{bin} = \frac{1}{N_{tot}}(E_{tot} - N_O E_O - N_{Zn} E_{Zn}) \qquad (١)$$

۳- ZnO Bernal graphenlike double layer, (BDL)

When a Zn atom in the first layer is set above of the O atom in the second layer, we have a ZnO Bernal graphenlike double layer, (BDL), Fig. ٦(a) shows this structure. The total energy of the BDL versus the interval of the two layers has showed in the Fig. ٦(b). As it' seen from the Fig. ٦(b), when distance of the layers is ۳,۲۱ Å, the system is in the stable state. Now in this inter layer distance, we calculation density of states and band structure. Band structure and density of states of BDL are showed in Figs.۷, ۸ respectively.

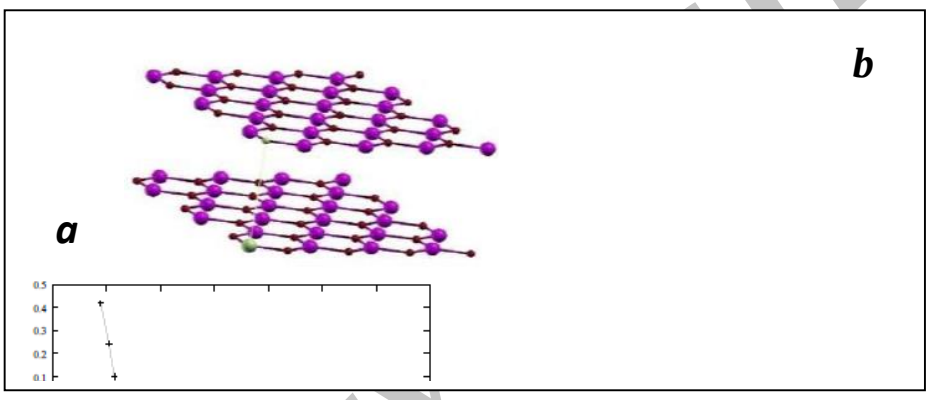


Fig.٦: a) ZnO Bernal graphenlike double layer, BDL, b): total energy of it vs. interlayer distance.

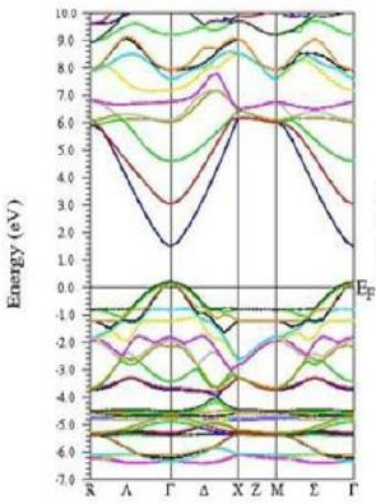


Fig. ۷: Band structure of BDL.

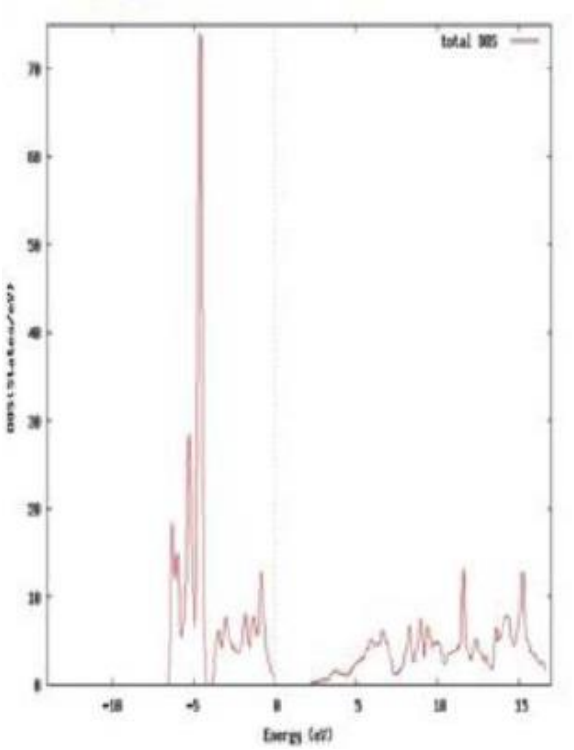


Fig. ۸: Density of states of BDL.

Figs. ۷, ۸ show the system has an energy gap about ۱،۳eV. In Fig. ۹ electronic density of BDL is seen. Hear, condense of electronic among of Zn atom and O atom is more than that SDL. Different of electronegativity of the Zn and O atoms is reason of this electronic density map.

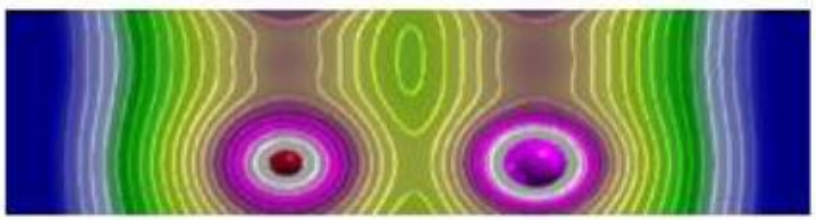


Fig. ۹: Electronic density of BDL.

Now we calculate the DOS of orbitals of O and Zn in the BDL. Because of energy gap of BDL is less than that of SDL and we want to find origin of it. Fig. ۱۰(a) shows the density of states, (DOS) of ۲s and ۲p oxygen orbitals. In Fig.۱۰(b) DOS of ٤s, ۳p and ۳d of Zn orbitals are seen. As one can seen the main contribution in reduce of the energy gap of BDL comes from ۳d orbital of Zn and ۲p orbital of O.

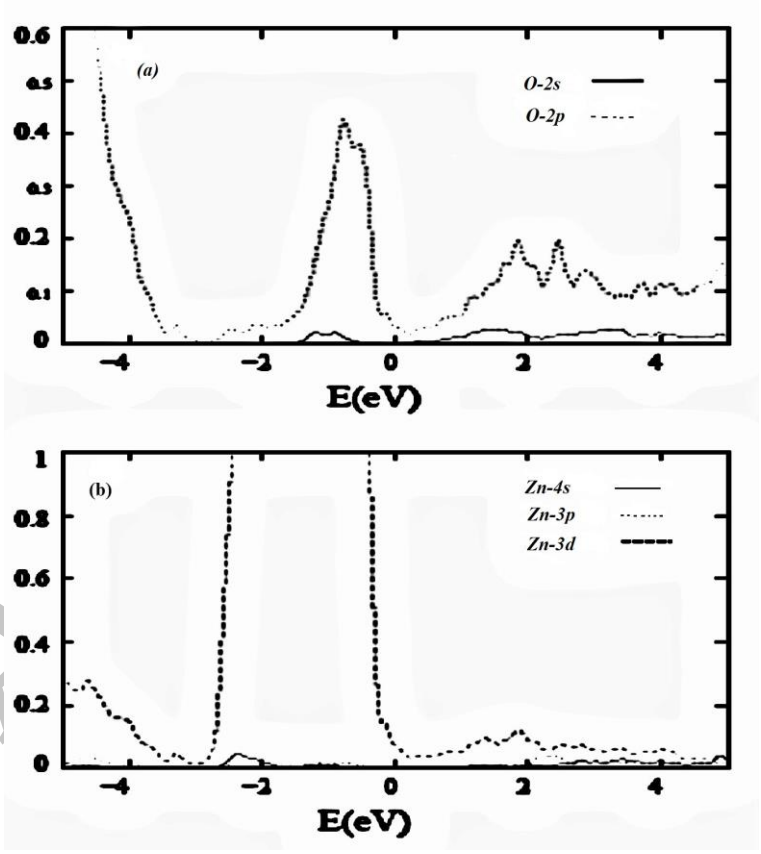


Fig. ۱۰: Partial density of states of O (a), and Zn (b) atoms in BDL.

٤-Zigzag ZnO nanoribbons

In ZnO graphenlike single layer, if we restrict the system in one direction, we'll have a nanoribbon. First ZnO nanoribbons with zigzag edge that their widths were ٤, ٥, ٦ hexagons considered. Fig. ١١ showes a supercell of this system with ٥ hexagons width. In this figure the violet, red and blue sphere show the Zn, O and H atoms respectively. Dangling bounds σ have saturated with H atoms. The bound lengths are Zn-H=١,٥٣Å, O-H= ٠,٩٧Å. These datas were obtained by relax of the system. To minimization of the forces, we considered the convergence of force parameter ١mRy/au. Figs. ١٢, ١٣, ١٤ show density of states of the system when their widthes are considered ٤, ٥, ٦ hexagon respectively. In all of three Figs. ١٢, ١٣, ١٤, there are peaks in the Fermi level and there was no energy gap between valance band and conduction band. Therfor these structures have metalic behavior. But the peak in Fig. ١٤ is higher than that the others. Then one can say with increase width of nanoribbon, density of states in Fermi level is increased too.

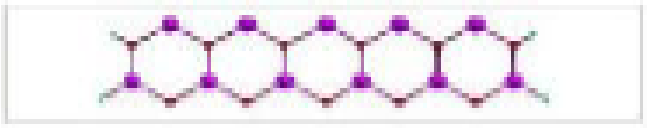
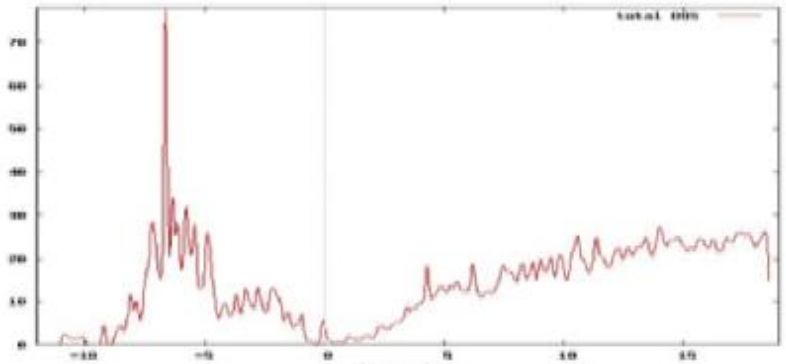


Fig.١١: A supercell of zigzag ZnO nanoribbon with ٥ width.



Energy (eV)

Fig.١٢: DOS of zigzag ZnO nanoribbon with ٤ hexagons width.

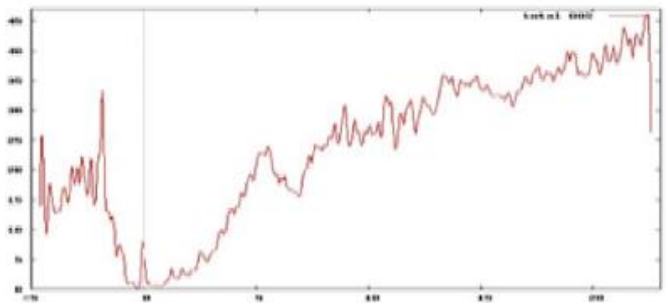


Fig.۱۳: DOS of zigzag ZnO nanoribbon
with ٥ hexagon width.

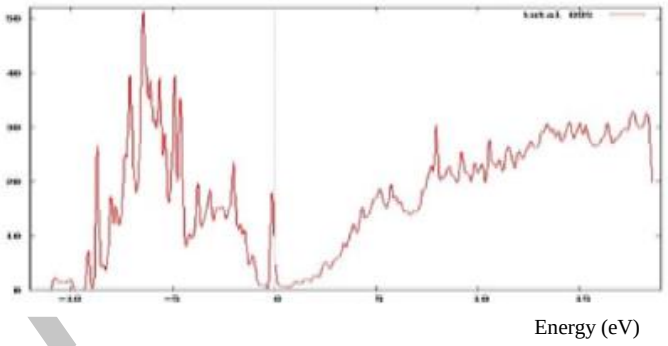


Fig.۱٤: DOS of zigzag ZnO nanoribbon
with ٦ hexagons width.

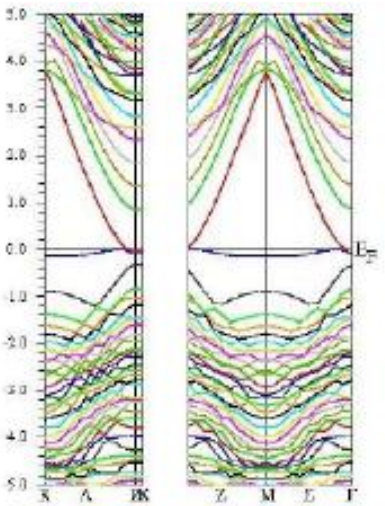


Fig.۱٥: BS of zigzag ZnO nanoribbon
with ٥ hexagons width.

٥- Armchair ZnO nanoribbons

A supercell of armchair ZnO nanoribbons is seen in Fig. ۱٦. Figs. ۱۷, ۱۸ show density of states and band structure respectively when width of the nanoribbon is considered ٤ haxagons. Indeed we studied different widthes of the system, and all of them showed semiconductor behavior. As one see from Figs. ۱۷, ۱۸ there is an energy gap in about Fermi level and it's equal to ۲،۱ eV, and it's in X point of Brillouin zone. Therfor this system has semiconductor property.

Fig.۱٦: A supercell of armchair ZnO nanoribbon.

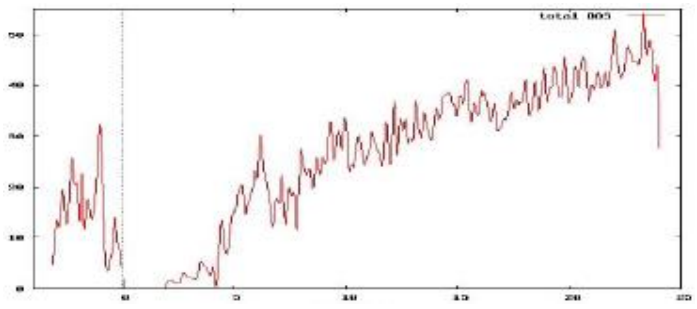


Fig.۱۷: DOS of armchair ZnO nanoribbon with
٤ hexagons width.

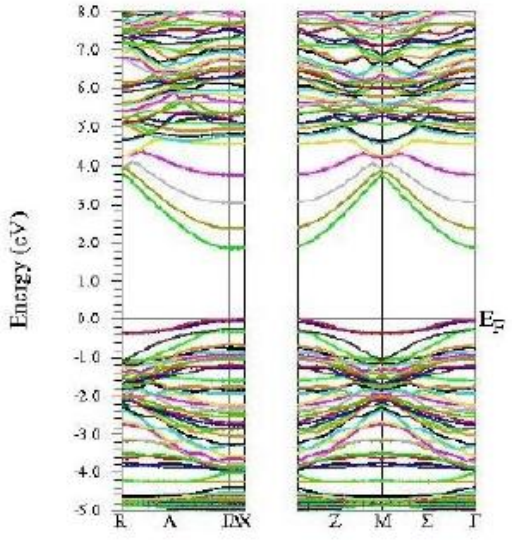


Fig.۱۸: BS of armchair ZnO nanoribbon
with ٤ hexagons width.

Conclusion

We have studied the electronic properties of ZnO graphenlike single layer, (SL), ZnO simple graphenlike double layer, (SDL), Zno Bernal graphenlike double layer, (BDL), zigzag ZnO nanoribbons with different widthes, and armchair ZnO nanoribbons. We found that these structures depend of their structures have different electronic properties, and the main contribution in the properties comes from ٣d of Zn and ٢p of O atoms.

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