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Design, Optimization, Structural and Electronic Properties of PVA/ZnO/SnO₂ Nanostructures for Nanoelectronics Fields

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This work aims to design the new polyvinyl alcohol (PVA)/zinc oxide (ZnO)/tin oxide (SnO₂) nanostructures as potential nanomaterials to utilize in numerous nanoelectronics devices. The optimization, structural and electronic properties of designed nanostructures are investigated. The results show that the electronic properties of PVA are enhanced by adding ZnO/SnO₂ nanostructures. The energy gap is reduced from 5.147 eV for PVA to 2.893 eV with adding ZnO/SnO₂ nanostructures. Finally, obtained results on electronic properties show that the PVA/ZnO/SnO₂ nanocomposites manifest excellent electronic properties, which made them as promising nanomaterials for nanoelectronics applications.

Цю роботу спрямовано на розробку нових наноструктур полівінілового спирту (ПВС)/оксиду Цинку (ZnO)/оксиду Стануму (SnO₂) як потенційних наноматеріялів для використання у багатьох пристроях наноелектроніки. Досліджено оптимізаційні, структурні й електронні властивості розроблених наноструктур. Результати показали, що електронні властивості ПВС поліпшуються завдяки додаванню наноструктур ZnO/SnO₂. Енергетична щілина зменшується від 5,147 еВ для ПВС до 2,893 еВ з додаванням наноструктур ZnO/SnO₂. Нарешті, одержані результати стосовно електронних властивостей показали, що нанокомпозити ПВС/ZnO/SnO₂ мають чудові електронні властивості, що робить їх перспективними наноматеріялами для застосування в наноелектроніці.

Key words: PVA, SnO₂, ZnO, nanocomposite, energy gap, nanoelectronics.

Ключові слова: полівініловий спирт, SnO₂, ZnO, нанокомпозит, енерге-

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тична щілина, наноелектроніка.

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1. INTRODUCTION

Recent years have seen a rise in the use of nanocomposite materials in scientific research, with the promotion of physical properties and changes in energy storage technologies as essential components for practical applications. The current applications of nanocomposites include high-energy batteries, fuel cells, microwave absorbers, optoelectronics, gas sensors, and UV filters [1]. Polyvinyl alcohol (PVA) is an atactic, semi-crystalline polymeric material that possesses excellent biodegradability, biocompatibility, useful mechanical properties, excellent optical properties, and non-toxicity, hence its wide range of applications. Other excellent properties of polyvinyl alcohol include thermal stability, water solubility, excellent optical transmission, and non-corrosiveness. These features, especially its optical properties such as the refractive index and energy gap, promote its industrial and technological uses as an optoelectronic material, a coating material, a solar cell component, a super capacitor component, and a component of several kinds of sensors [2].

Because of its large exciton binding energy (60 meV) and direct band gap energy (3.37 eV), the applications of heterostructure based on zinc oxide attracted great interest [3]. ZnO is an interesting semiconductor for development of many advanced technologies because of its direct wide band gap and optical transparency, which lead to good optical and electronic properties. They are promising candidates in flat panel displays to see through front faced electrodes, light-emitting devices, solar cell and gas sensors [4].

Tin oxide (SnO_2) is an *n*-type semiconductor that possesses a high optical gap (3.6-4.0 eV) and has a variety of applications. Some of these applications include secondary lithium batteries, solar cells, gas sensors, and glass electrodes. It has a structure known as tetragonal rutile, and the inherent oxygen vacancies in this structure operate as an *n*-type dopant [5].

There many studies on metal oxides doped polymers to apply in various electronics and optical fields [6–10]. This work aims to design of $PVA/ZnO/SnO_2$ nanocomposites as potential nanomaterials to use in many nanoelectronics fields.

2. COMPUTATIONAL DETAIL

In this work, all the geometric structures are optimized and consid-

ered by density functional theory (DFT) with B3LYP [11] functional and the 6-31G (d) basis set, which applied in Gaussian 09 software [12]. This chemical model has been extensively used to relax the geometry and calculate the optoelectronic properties, such as total energies (E_T), Fermi level energy (E_{Fl}), orbital distributions (HOMO, LUMO), energy gap (E_g), and electronic-transition energies. These methods are not only encouraging more profound understanding of the association between the optoelectronic properties and chemical structures of the molecule structures but also may be used to design new molecule structures. To evaluate the reactivity and the stability of the composites, DFT-based descriptors were calculated [12, 13]:

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{V(\mathbf{r}), T},\tag{1}$$

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{V(\mathbf{r}), T},$$
(2)

$$S = \frac{1}{2\eta} , \qquad (3)$$

$$\omega = \frac{\mu^2}{2\eta} \tag{4}$$

with I_P , E_A , μ , η , S, and ω —the ionization potential, electron affinity, chemical potential, chemical hardness, chemical softness, and electrophilicity, respectively, while E, N and $V(\mathbf{r})$ are the total electron energy, number of electrons, and external potential, respectively. There are two different methods to calculate the above the global quantities. The first is a finite difference approximation, which based on the differences of total electronic energies, when an electron is removed or added in accordance with the neutral molecule.

The second is Koopmans' theorem, which based on the differences between the HOMO and LUMO energies for the neutral molecule [12]. Using a finite difference approximation, the global quantities can be given by [14-16] as follow:

$$I_{P} = -E_{\text{HOMO}}, \ E_{A} = -E_{\text{LUMO}}, \ \eta = \frac{(I_{P} - E_{A})}{2}.$$
 (5)

Then, using Koopmans' theorem, the above equations can be given as follow:

$$E_{Fl} = \frac{E_{HOMO} + E_{LUMO}}{2}, \ \eta = \frac{E_{HOMO} - E_{LUMO}}{2}.$$
 (6)

3. RESULTS AND DISCUSSION

The molecules studied are represented in Figs. 1, 2. Computational analyses were performed using the Gaussian 09 suite of programs [11, 15] and the density functional theory (DFT) methods.

Figures 2 and 3 display the geometrical optimization of the suggested structures investigated in this research after relaxing. These structures include polyvinyl alcohol (PVA), and PVA-ZnO-SnO₂. The studied-geometry optimization yielded results, which agree well with experimental data, particularly, in terms of the composites' structural properties. The relaxed structures under examination exhibited carbon-carbon-bond lengths within the ranges of C-C: 1.534 Å, C=C: 1.361 Å, C=C: 1.422 Å, C-H: 1.092 Å, C-O: 1.23 Å, O-H: 0.978 Å, Zn-O: 1.98 Å and Sn-O: 2.012 Å, as shown in Figs. 2 and



Fig. 1. Structure of PVA before relaxing.



Fig. 2. Structure of PVA after relaxing.



Fig. 3. Structure of PVA-ZnO-SnO₂ composites.

3. These findings are consistent with the bond lengths observed in aromatic rings [12, 13].

The atoms bonded to carbon and oxygen can vary in type, size, and electronic effects, and the presence of different atoms (Zn, Sn) adjacent to carbon and oxygen can lead to changes in the chemical environment and consequently affect the bond length. Oxidation of carbon or oxygen in the molecule can also influence the chemical environment and, consequently, the bond length. For example, the carbon in the C=O bond in ketones may have a different oxidation state compared to the carbon in the C-O bond in alcohols. Additionally, interactions between adjacent molecules and electrostatic forces between them can also affect the bond length. The presence of positive or negative electrostatic charges in neighbouring molecules can influence electron transfer, and factors such as transition-state effects, hydrogen-bonding interactions, and bond polarization can influence the bond length too. All of these factors contribute to determining the bond length between carbon and oxygen in organic molecules [13–15].

The Geometrical Optimization of Polymeric Composites, PVA and $PVA-ZnO-SnO_2$. It possesses structural properties, which agree well with the experimental data in terms of bond length and bond strength, and this indicates that these materials show interactions and properties that are well compatible with each other from the physical and chemical points of view as shown in Fig. 3. This means

that they are able to interact with each other effectively and form new compounds or compounds in a consistent and homogeneous manner. This compatibility indicates that the said materials may be suitable for use in joint applications or in forming composite compositions that benefit from their combined interactions [11, 12, 16].

Table shows the ground state calculations of the polymeric composites in this work at the minimum energy. These calculations are included the total energy in a.u., I_P and E_A in [eV] calculated due to Koopmans' theorem, forbidden energy gap E_g in [eV], S in [eV⁻¹], η in [eV], μ in [eV], and ω in [eV]. In addition, the calculations are included the density of states (DOS), HOMO energies (E_{HOMO}) and LUMO energies (E_{LUMO}).

The total energy E_T of polymeric composites under study is very small; this result is a reflection of the binding energy of each structure. Thus, polymeric composites with lower total energy may have limited energy storage capabilities. This is due to the specific material selection or composition of the composites that is desirable in some applications where lightweight materials are required [11, 17].

In addition, both the I_P and the E_A differ in value, where I_P and E_A for PVA-ZnO-SnO₂ are higher than for PVA. A higher value indicates that the material has a stronger tendency to retain its electrons (higher ionization potential) or to attract additional electrons (higher electron affinity). These differences in electronic properties can arise from variations in the chemical composition, structure, or bonding characteristics of the polymeric composites. Factors such as the presence of different functional groups, molecular weight, or the arrangement of atoms within the composite can influence these electronic properties [13, 18].

The above results are corresponding to S, η and ω of the structures PVA and PVA–ZnO–SnO₂; the results showed that the polymeric composites has large value of η and ω . This indicates a greater energy requirement meaning that the system is relatively more stable and less reactive towards electron transfer, while small value of S, whereas shown in Table. But, for PVA and PVA–ZnO–SnO₂, the value of chemical hardness and electrophilicity decreases, while the chemical softness increases, and this is due to the compatibility and good distribution of materials within the polymer, where you indicate higher values of chemical softness indicating a lower energy requirement for electron transfer, implying higher reactivity, and a greater tendency to undergo electronic changes [14, 19].

The results indicate a decrease in the E_g values, when adding $ZnO-SnO_2$ to PVA. This is an indication of the closeness of the HOMO and LUMO values to each other and, thus, the possibility of an electronic transition between the valence band and the conductivity one.

Fermi level en hardness (η) , ch units of $[eV]$.	ergies (E_{F}) , nemical soft	, ionizatio ness (S) a	n potentia nd electrop	$\begin{bmatrix} (I_p), e \end{bmatrix}$	ectron af ndex (w) v	finity (E_{A}) via using]), chemica DFT B3L	al potenti YP/6-31 (al (µ), c d) calcula	hemical ation in
Sample	$oldsymbol{E}_{T}$	OMOH	LUMO	$E_{_g}$	I_{P}	E_{A}	$oldsymbol{E}_{_{Fl}}$	μ	S	8
PVA	-7325.547	-7.801	-2.654	5.147	7.801	2.655	-5.22	2.573	0.194	5.311
PVA-ZnO-SnO ₂	-5325.278	-5.147	-2.254	2.893	5.148	2.255	-3.70	1.446	0.346	4.735
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In addition, when these materials are added to the polymer, they interact and interfere with the existing polymer structures. This reaction leads to the formation of new energy states within the polymer, and these states are less energetic than the original states that results in a decrease in the value of the energy gap [12, 14].

Through Figs. 4 and 5, one can see that the HOMO and LUMO for the $PVA-ZnO-SnO_2$ are more stable in comparison with PVA. There is a clear difference in the electronic distribution of shipments due to the withdrawal of shipments. HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) are commonly used in the field of molecular orbital theory



Fig. 4. The shapes of HOMO and LUMO for PVA.



Fig. 5. The shapes of HOMO and LUMO for PVA-ZnO-SnO₂ composites.

to describe the energy levels of electrons within the molecule. These energy levels play a significant role in determining the chemical and physical properties of the molecule [14, 20, 21].

The HOMO represents the highest energy level occupied by electrons in a molecule in its ground state; it corresponds to the valence electrons, which are involved in bonding and determining the reactivity of the molecule. The energy of the HOMO is an indicator of the molecule ability to donate electrons during chemical reactions. Figures 4 and 5 show the shapes of HOMO and LUMO for these structures drawn by Gaussian View 5.0.8 using B3LYP/6-31G (d) method.



Fig. 6. Density of states (DOS) for PVA.



Fig. 7. Density of states (DOS) for PVA–ZnO–SnO₂ composites.

The DOS provides valuable insights into the electronic structure and properties of materials. It helps determine various properties, such as electrical conductivity, thermal conductivity, and optical properties. By analysing the DOS, one can study phenomena like band gaps, energy bands, and Fermi energy, which are essential for understanding the behaviour of electrons in solids.

The DOS is typically represented as a function of energy, denoted as g(E), where E represents the energy level. It describes the number of states per unit volume per unit energy range at a particular energy level. Mathematically, the DOS can be expressed by [12, 15] as follows:

$$g(E) = (1/V)dN(E)/dE,$$

where V is the volume of the material and dN(E)/dE represents the change in the number of states with respect to energy.

Through the density diagram of the polymeric compounds and, as shown in Figs. 6 and 7, there is a clear energy gap between the valence band (the highest occupied energy band) and the conduction band (the lowest unoccupied energy band). In DOS, this results in a region of zero or a very low density of states within the band gap. The DOS is relatively high in the valence and conduction bands, indicating the availability of occupied or excited electronic states.

4. CONCLUSION

The current study includes design of $PVA/ZnO/SnO_2$ nanocomposites as new nanomaterials to utilize in numerous nanoelectronics devices. The optimization of structural and electronic characteristics of $PVA/ZnO/SnO_2$ nanocomposites is studied. The results demonstrated that the electronic characteristics of PVA were enhanced with adding ZnO/SnO_2 nanostructures. The energy gap reduced from 5.147 eV for PVA to 2.893 eV with adding ZnO/SnO_2 nanostructures. The final results indicate that the PVA/ZnO/SnO₂ nanostructures that the PVA/ZnO/SnO₂ nanostructures have excellent electronic characteristics, which made them as promising nanomaterials for nanoelectronics fields.

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