

PACS numbers: 71.15.Nc, 71.20.Rv, 78.30.Jw, 78.40.Me, 78.67.Sc, 81.07.Pr, 85.65.+h

Tailoring the Structure, Electronic and Optical Properties of PEO/CuO/In₂O₃ New Structures for Flexible Electronics and Optics Approaches

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The new polyethylene oxide PEO–copper oxide CuO–indium oxide In₂O₃ structures are designed to use in various optics and electronics approaches. The structure, optical and electronic properties as well as optimized geometry for PEO–CuO–In₂O₃ structures are studied by using DFT at the B3LYP level with basis set SDD. The electronic characteristics at issue contain total energy, cohesive energy, HOMO, LUMO, ionization potential, energy gap, softness, electronic affinity, hardness, electronegativity, and electrophilicity. The results indicate that the optical and electronic properties of PEO are enhanced with adding of the CuO/In₂O₃ nanostructures. The energy gap is found of 8.06 eV for pure PEO and 2.35 eV for PEO–CuO–In₂O₃ nanostructures. Finally, the results of studied characteristics show that the PEO–CuO–In₂O₃ structures can be used in different low-cost and flexible-optoelectronics applications.

Розроблено нові структури поліетиленоксид (ПЕО)–оксид Купруму (CuO)–оксид Індію (In₂O₃), призначені для використання в різних підходах до оптики й електроніки. Структура, оптичні та електронні властивості, а також оптимізована геометрія для структур ПЕО–CuO–In₂O₃ вивчаються за допомогою теорії функціоналу густини на рівні B3LYP з базисним набором SDD. Електронні характеристики, про які йде мова, містять повну енергію, енергію когезії, НОМО, LUMO, потенціал йонізації, енергетичну щільність, м'якість, електронну спорідненість, твердість, електронегативність та електрофільність. Результати свідчать про те, що оптичні та електронні властивості ПЕО поліпшуються за рахунок додавання наноструктур CuO/In₂O₃. Енергетична щільність виявляється у 8,06 еВ для чистих ПЕО і у 2,35 еВ для наноструктур ПЕО–CuO–In₂O₃. Нарешті, результати досліджу-

ваних характеристик показують, що структури PEO–CuO–In₂O₃ можуть використовуватися в різних недорогих застосуваннях і, зокрема, у так званій і гнучкій оптоелектроніці.

Key words: In₂O₃, CuO, PEO, optical characteristics, electronics fields, DFT, DFT–B3LYP/SDD level of calculations.

Ключові слова: In₂O₃, CuO, поліетиленоксид, оптичні характеристики, розділи електроніки, теорія функціоналу густини, розрахунковий рівень B3LYP/SDD.

(Received 7 May, 2022)

1. INTRODUCTION

The polymer matrix doped with nanoparticles, nanoscale sheets, nanotubes, *etc.* are called nanopolymer compounds; the physical properties of these nanocomposites are mostly dependent on polymer molecules in contact with nanofillers [1]. Nanomaterials have received much attention among materials, and their properties depend not only on their composition but also on their shape, size distribution [2]. Polymers and organic materials have received a lot of attention due to their unique features that provide lightweight, environmentally friendly, flexible and cost-effective electronic devices [3]. Organic polymer-based materials are very important in the field of optoelectronics due to their attractive properties [4]. The addition of inorganic nanoparticles to polymers allows modification of the physical properties of the polymer as well as the implementation of new features of the polymer matrix [5]. Polyethylene oxide is known to create molecular complexes with alkali metal salts. They manifest themselves as large ionic conductors and are recognized as electrolyte solid polymers. Therefore, they have attracted attention in recent years due to their water solubility, non-toxicity, and biocompatibility. It has many applications, such as agricultural films, paper coating, textile fibres, and electronic devices [6]. CuO has attracted a lot of attention too. CuO is a *p*-type semiconductor material with small band-gap energy of only 1.2 eV at room temperature; it has been proven that CuO can be used in high-temperature superconductors, gas sensor, magnetic storage media, catalysis, and field emission [7]. With metallic nanoparticles, copper oxide nanoparticles CuO NPs are of great importance according to their ability to interact effectively with light through dint of surface plasmon resonance (SPR) [7, 8]. The organics doped with inorganic nanoparticles have been focused for their excellent chemical, physical characteristics, huge potential applications in nanoelectronic devices and other fields [5–8]. In this paper, design of novel PEO–Cu–In₂O₃ structures for electronic and optic applications is considered.

2. THEORETICAL PART

Cohesive energy is defined as the energy required for separating condensed matter into separate atoms [9]:

$$E_{coh} = (E_{tot}/n) - E_{free} - E_0, \quad (1)$$

where E_{tot} is the total energy, E_{free} is the energy of free atoms, n is a number of atoms, E_0 is the vibrational energy of ground states (zero-point). HOMO (the highest energy orbital occupied by the electrons) and LUMO (the lowest energy orbital unoccupied by the electrons) are two essential components in calculating properties such as the molecular interactions and the ability of the molecule to absorb a photon of light. According to Koopmans' theorem [10], the band gap is obtained as:

$$E_g = E_{LUMO} - E_{HOMO}. \quad (2)$$

The ionization potential (IP) varies between the positive energy $E_{(+)}$ and the neutral energy $E(n)$:

$$IP = E_{(+)} - E(n). \quad (3)$$

The electron affinity (EA) is given by the equation:

$$EA = E(n) - E_{(-)}. \quad (4)$$

The energies of the boundary orbitals are determined as follow:

$$IP = -E_{HOMO}, \quad (5)$$

$$EA = -E_{LUMO}. \quad (6)$$

Chemical hardness (η) is a measure of the resistance to charge transport. It is given as a function of the numbers of electrons N and the external voltage $V(r)$ [11]:

$$\eta = \frac{1}{2} \left[\frac{\partial^2 E}{\partial N^2} \right]_V = \frac{1}{2} \left[\frac{\partial \mu}{\partial N} \right]_V = \frac{1}{2} \left[\frac{\partial X}{\partial N} \right]_V, \quad (7)$$

$$\eta = (IP - EA)/2. \quad (8)$$

Chemical fineness (S) is a feature of the molecules that gives the degree of a chemical reaction. It is opposite to chemical hardness (η) [12]:

$$S = \frac{1}{2\eta} = \left[\frac{\partial^2 N}{\partial E^2} \right]_V = \left[\frac{\partial N}{\partial \mu} \right]_V, \quad (9)$$

The chemical potential μ is defined as [15]:

$$\mu = [\partial E / \partial N]_V, \quad (10)$$

where V —nuclei potential. Then, we can determine the electronegativity using the relationship [11]:

$$X = -\mu = -[\partial E / \partial N]_V. \quad (11)$$

It can be obtained by the average ionization energy and electron affinity [9]:

$$X = (IP + EA)/2. \quad (12)$$

According to Koopmans' theorem, 'it is defined as the negative value for average of the energy levels of the HOMO and LUMO' [13]:

$$X = -(E_{\text{HOMO}} + E_{\text{LUMO}})/2. \quad (13)$$

It measures the energy stability, when the structure gets additional electron charges from the environment defined as electrophilic [14]:

$$\omega = \mu^2 / (2\eta). \quad (14)$$

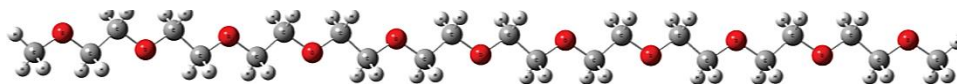


Fig. 1. Optimization of PEO structure.

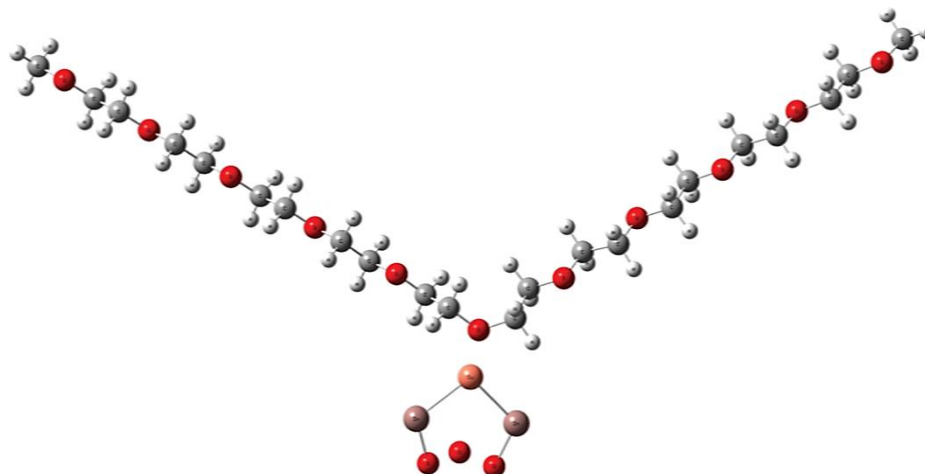


Fig. 2. Optimization of PEO-CuO-In₂O₃ structure.

3. RESULTS AND DISCUSSION

Figures 1 and 2 show the optimized structures of PEO and PEO–CuO–In₂O₃. Structures were optimized within the DFT scope using ‘three-parameter hybrid functional’ of Becke B3LYP and 6-31G basis sets. These results are consistent with Refs. [15–17].

Figures 3 and 4 show the IR spectra of the PEO and PEO–CuO–In₂O₃ structures obtained using density functional theory. The FTIR studies show that adding CuO–In₂O₃ leads to the displacement of some of the bonds and not emergence of new peaks [18–20].

Figures 5 and 6 show the UV–Vis spectra. Visible and ultraviolet spectra are relevant to the electronic structure of the molecules. From Figures 5 and 6, absorption intensity for the PEO–CuO–In₂O₃ structures has higher UV–Vis spectra. As a result, it shows that absorption increases with increasing the number of atoms. This is

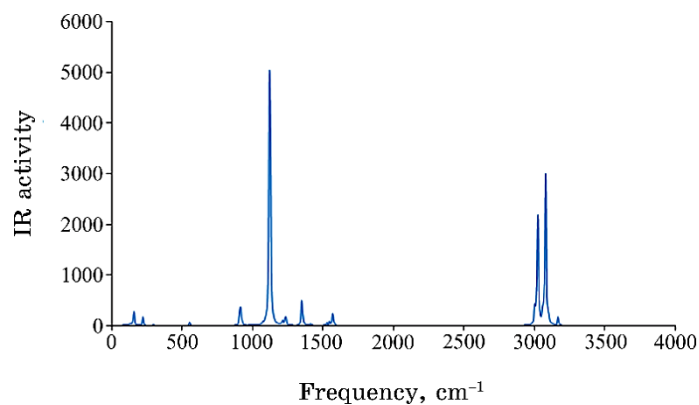


Fig. 3. IR spectra of PEO structure.

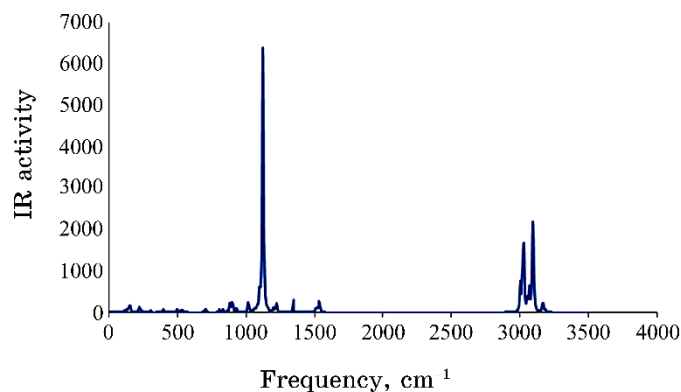


Fig. 4. IR spectra of PEO–CuO–In₂O₃ structure.

owing to the moving electrons from valence level to the conduction band at these energies; hence, the increase in absorption is due to the increase in a number of charges' carriers [21–24].

Table 1 represents the comparison between the E_g values for the PEO and PEO–CuO–In₂O₃ structures. From the results, the energy gap calculated decreases with increasing the number of atoms.

Figures 7 and 8 illustrate the 3D distribution of HOMO and LUMO for the studied composites.

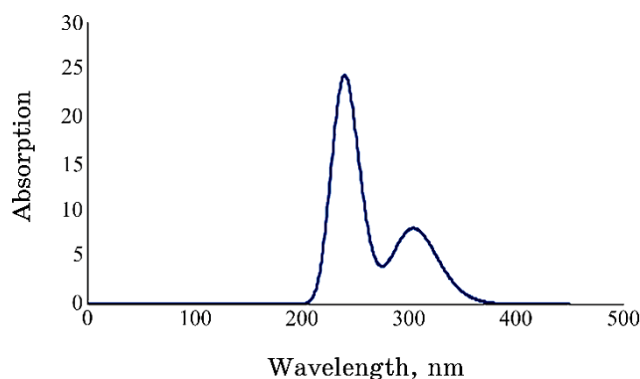


Fig. 5. UV–Vis spectrum for PEO structure.

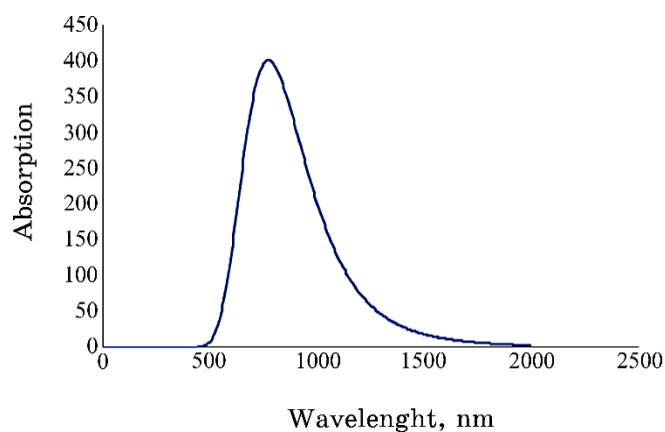


Fig. 6. UV–Vis spectrum for PEO–CuO–In₂O₃ structure.

TABLE 1. The values of energy gap (in eV) of the studied structures.

PEO structure			PEO–CuO–In ₂ O ₃ structure		
E_{HOMO} , eV	E_{LUMO} , eV	E_g , eV	E_{HOMO} , eV	E_{LUMO} , eV	E_g , eV
-6.7995	1.2679	8.0674	-4.4850	-2.1327	2.3523

Table 2 shows the energies (in a.u.) and some electronic properties of the PEO and PEO–CuO–In₂O₃ structures calculated at the same level of theory. These properties are including IE , EA , E_N , η and ω .

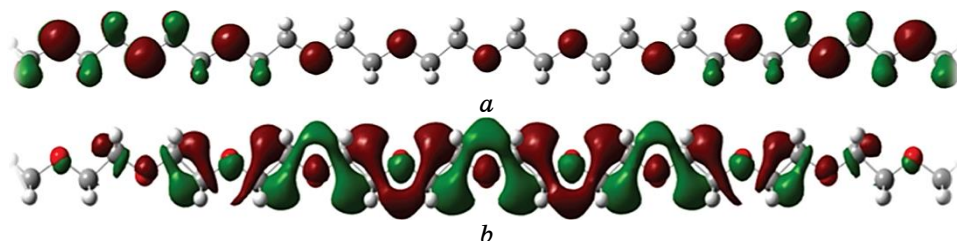


Fig. 7. The distribution of HOMO (up) and LUMO (down) for PEO.

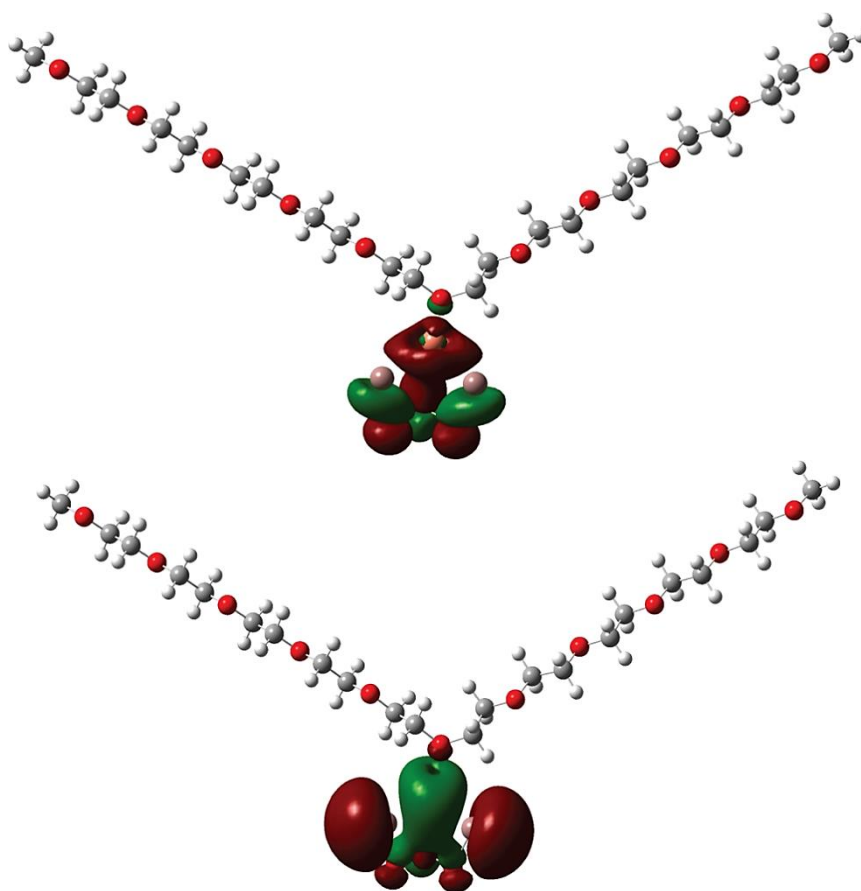
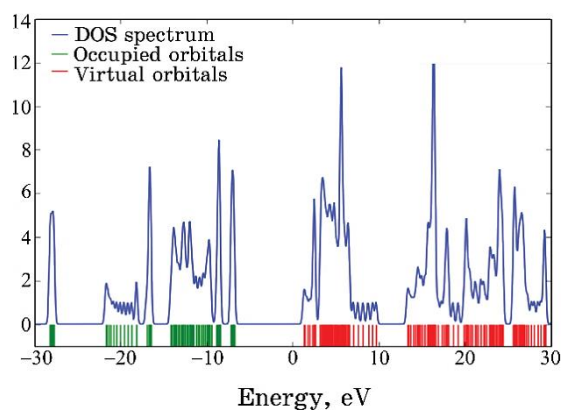
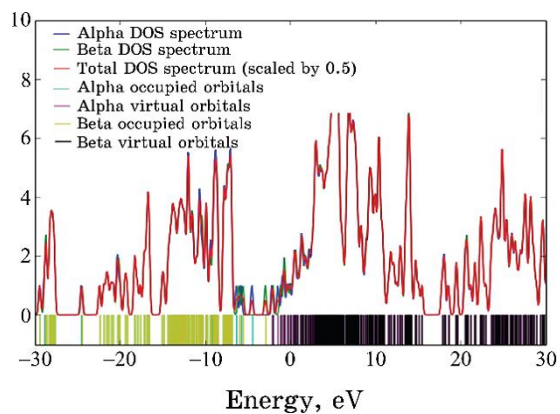


Fig. 8. The distribution of HOMO (up) and LUMO (down) for PEO–CuO–In₂O₃ structure.

TABLE 2. Electronic properties' values (in eV) for the structures.

Property	PEO	PEO-Cu-In ₂ O ₃ composites
Cohesive energy	-4.7379	-16
Total energy	-1692.8063	-2119.8614
Ionization potential	6.7995	4.4850
Electron affinity	-1.2679	2.1327
Electronegativity	2.7658	3.3088
Chemical hardness	4.0337	1.1761
Chemical softness	0.1239	0.4251
Chemical potential	-2.7658	-3.3088
Electrophilicity	0.9482	4.6544
Dipole moment (Debye)	1.6673	5.5244

**Fig. 9.** DOS of PEO structure.**Fig. 10.** DOS of PEO-CuO-In₂O₃ structure.

Density of states (DOS) for the PEO and PEO–CuO–In₂O₃ structures *versus* energy levels were calculated by employing the DFT–B3LYP/SDD level as presented in Figs. 9 and 10. From DOS spectrum, the charge density is low in occupied orbital and high in virtual orbital for pure, O- and H-substituted In₂O₃ structures. As shown, the PEO–CuO–In₂O₃ composite has a doublet state, while the others have a singlet state. In this case, the degeneracies of unoccupied molecular orbitals are more than for the occupied molecular orbitals. The bonds are mainly formed by hybridization between the O_{PEO} orbital and the CuO and In₂O₃ orbitals.

4. CONCLUSIONS

This paper includes design of novel PEO–CuO–In₂O₃ structures. The structure, optical and electronic properties as well as optimized geometry for the PEO–CuO–In₂O₃ structures were studied. The density functional theoretical methodology has been proved its validity in calculating the geometrical parameters for the PEO–CuO–In₂O₃ structures. The energy gap of PEO–CuO–In₂O₃ is equal to 2.352 eV that makes it suitable for different optoelectronics devices. The total cohesive energy (absolute value) increases with adding the CuO–In₂O₃. The results show that the PEO–CuO–In₂O₃ structures can be used in various low-cost, high corrosion resistance, lightweight and flexible-optoelectronics applications.

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