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Exploring the Optical, Electronic and Thermal Characteristics of (PEO/Cu/Ag/H_2O) New Nanostructures to Use in Solar Collectors

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The present paper aims to design of new (PEO–Cu–Ag–H_2O) nanostructures to use it in solar collectors with high dispersion of metallic particles, good solar energy absorption and high corrosion resistance. The theoretical method of DFT offers nanostructures and energies. The structural stability and electronic properties of the nanostructures are studied in relations of the calculated energy, ionization potentials, HOMO–LUMO gap, and electron affinity. A dipole moment of (PEO–Cu–Ag–H_2O) nanostructures is also determined. The results show that the (PEO–Cu–Ag–H_2O) nanostructures have good structure, optical, electronic and thermal properties. The PEO–Cu–Ag–H_2O nanostructures have high absorption of solar energy at wavelength in a range 200–350 nm. Finally, the results indicate that PEO–Cu–Ag–H_2O structures may be used in renewable energy field for solar collectors.

Дану роботу спрямовано на розробку нових наноструктур (PEO–Cu–Ag–H_2O) для використання їх у сонячних колекторах з високою дисперсністю металевих частинок, хорошим поглинанням сонячної енергії та високою корозійною стійкістю. Теоретичний метод ТФГ пропонує наноструктури та енергії. Вивчаються структурна стійкість та електронні властивості наноструктур стосовно розрахункової енергії, потенціялів йонізації, щілини HOMO–LUMO та спорідненості електронів. Також визначено дипольний момент наноструктур (PEO–Cu–Ag–H_2O). Результати показують, що наноструктури (PEO–Cu–Ag–H_2O) мають хороші структурні, оптичні, електронні та теплові властивості. Наноструктури PEO–Cu–Ag–H_2O мають високе поглинання сонячної енергії на довжині хвилі в діяпазоні 200–350 нм. Нарешті, результати вказують на те, що структури PEO–Cu–Ag–H_2O можуть використовуватися у сфері відновлюваної енергії для сонячних колекторів.

Key words: PEO, copper, solar collectors, polarizability, absorption, electronic properties.

Ключові слова: поліетиленоксид, мідь, сонячні колектори, поляризовність, вбирання, електронні властивості.

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1. INTRODUCTION

Polymers are versatile materials that have certain unique properties such as low density, flexibility, toughness, easy processability, and low conductivity. However, these properties are still inadequate for efficient industrial applications. Hence, continuous research efforts are in progress to develop new polymeric materials with advanced properties. The desired properties can be obtained by adding filler (organic and inorganic materials) to the polymer matrix. Common fillers such as metal particles, silica, carbon black, *etc.* require high filler loading. High filler loading increases the cost of composites along with challenging processability. Nowadays, nanofillers are incorporated in polymer matrixes to introduce desired properties with low filler loading [1]. Polyethylene oxide (PEO) can be considered as a semi-crystalline polymer with both amorphous and crystalline phases. The PEO can be distinguished through its high thermal and chemical stability, high viscosity, and non-ionic, heat formative, good water-solubility properties. PEO can also be identified through its flocculent thickening sustained-release lubrication that disperses fibres and retains water. Polyethylene oxide is a simple copolymer matrix that has enteric contacts [2].

The PEO is one of the flocculating systems, which is more effective than charged polymers in highly contaminated closed systems[3]. Metals' nanostructures have been paid much attention in the development of sensing devices due to their divergent physical and chemical properties [4]. Gaussian 03 program (computer software, which is capable of predicting many properties of molecules and reactions, including the molecular energies and structures) [5] is used to make the calculation. This paper aims to design of new (PEO–Cu–Ag–H_2O) nanostructures to use it in solar collectors.

2. THEORETICAL PART

Energy gap refers to energy difference between the (HOMO) and (LUMO) according to the Koopmans' theorem [6]:

$$E_{gap} = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}; \quad (1)$$

here, E_{gap} indicates the energy gap; E_{LUMO} and E_{HOMO} are denoting the energies of HOMO and LUMO in consecution.

Ionization energy is expressed in units of electron-volt (eV) by the equation [7]:

$$I_E = -E_{\mathrm{HOMO}}. \tag{2}$$

Electron affinity can be determined by the relation [6]:

$$E_A = -E_{\mathrm{LUMO}}. \tag{3}$$

One of the global quantities is chemical potential, which is given by the equation [8]:

$$\mu \approx \frac{1}{2}\left(E_{\mathrm{HOMO}} + E_{\mathrm{LUMO}}\right) \approx -\frac{1}{2}\left(I_E + E_A\right). \tag{4}$$

Chemical hardness is the resistance of species to lose electrons. It can be calculated as follows [9]:

$$H = \left(I_E - E_A\right)/2. \tag{5}$$

Chemical softness is the inverse with hardness [10]:

$$S = \frac{1}{2H}. \tag{6}$$

Electrophilicity can be defined as a measure of energy lowering due to maximal electron-flow between donor and acceptor [11]:

$$\omega = \frac{\mu^2}{2H}. \tag{7}$$

R. Mulliken defined electronegativity as the average of the ionization energy and electron affinity as follows [10]:

$$E_N = -\left(I_E + E_A\right)/2. \tag{8}$$

The polarizability is calculated by the following equation [12, 13]:

$$\langle\alpha\rangle = \left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right)/2. \tag{9}$$

There are many studies on properties of nanostructures to employ them in various applications and fields like electronics and optoelectronics [14–33], sensors [34–39], antibacterial agents [40–42], optical fields [43–47], bioenvironmental and radiation shielding fields [48–54], and thermal energy storage [55–56].

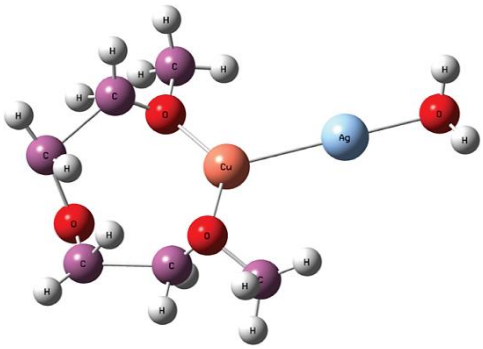

Fig. 1. Optimization of (PEO–Cu–Ag–H_2O) nanostructure.

TABLE 1. Average lengths of bond (in Å) and the angles in degree.

Measurements	Optimization parameters	Values
Bonds, Å	(C–C)	2.489
	(C–O)	1.497
	(C–H)	1.096
	(O–H)	0.973
	(Cu–O)	1.801
	(Ag–O)	2.238
Angles, deg.	(C–C–C)	122.136
	(H–O–H)	112.792
	(O–Cu–O)	172.018
	(Cu–0 –Ag)	108.274

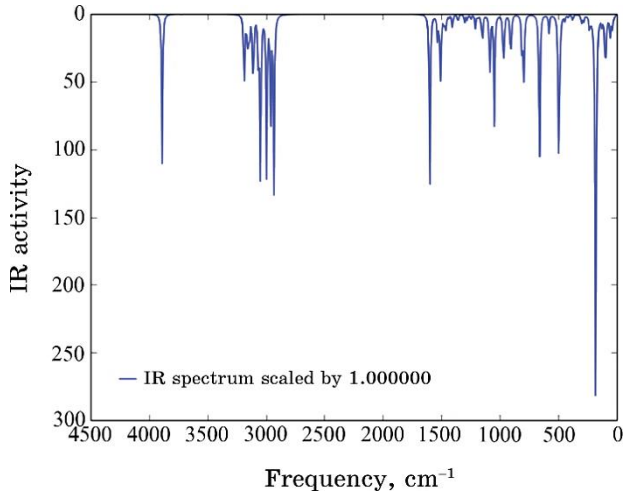

Fig. 2. IR spectra of the (PEO–Cu–Ag–H_2O) nanostructures.

3. RESULTS AND DISCUSSION

Figure 1 shows the relaxation of the (PEO–Cu–Ag–H_2O) nanostructures, in which the optimized structure of the molecule is the structure at minimum energy, and it is performed by finding the first derivative of the energy with respect to distance between different atoms.

Table 1 represents the standard orientation of all atoms in the molecule. The bonds values in present work are in a well agreement with Refs. [3, 57, 58].

Figure 2 shows the IR spectrum of the (PEO–Cu–Ag–H_2O) nanostructures obtained using DFT. It has been found that the strong peak observed at 300 cm^{-1} is attributed to the H_2O molecule and Cu–Ag bond.

In Raman spectrum, a different is observed in the molecules' polarization. Namely, interactions of ultraviolet or visible photons with vibrations of molecular bonds, losing or gaining parts of its energy, thereby, produce the spectra [59].

Figure 3 represents the Raman spectrum of the PEO–Cu–Ag–H_2O nanostructures. Raman spectrum intensities depend on the probability that photon with exacting wavelength will be absorbed.

Figure 4 gives the UV–Vis spectrum of the (PEO–Cu–Ag–H_2O) nanostructures. It is dependent on the molecule electronic structure. The results of UV–Vis spectrum for the (PEO–Cu–Ag–H_2O) nanostructures are found from the B3LYP-TD/LanL2DZ method integrating the wavelength, excitation energy, oscillator strength and electronic transition.

Table 2 gives the energy gap for the (PEO–Cu–Ag–H_2O) nanostructures. The energy gap did not only decide the path of interactions of molecule with other species, but also helps to illustrate the kinetic stability and chemical reactivity of the molecules like in metal complexes.

Figure 5 represents the 3*D* distribution of LUMO and HOMO for the (PEO–Cu–Ag–H_2O) nanostructures. The idea of HOMO–LUMO clearly characterizes the electron cloud in the virtual and occupied orbitals.

Figure 6 represents the distribution of electrostatic potential surfaces (EPS) for the PEO–Cu–Ag–H_2O nanostructures intended from the total self-consistent field. EPS distributions for the (PEO–Cu–Ag–H_2O) nanostructures are caused by repulsive forces or attracting regions around each structure. Mostly, the EPS for the (PEO–Cu–Ag–H_2O) nanostructures in each molecule determine the high electronegativity of oxygen atoms (3.5 eV), which are dragged toward the negative charges positions.

Table 3 represents the results for the ground state energy and

several electronic characteristics of (PEO–Cu–Ag–H_2O) nanostructures calculated at the same level of theory. These characteristics are including the I_E, E_A, E_N, H and ω.

Table 4 shows the average polarizability α_{ave} (9) and its components for the PEO–Cu–Ag–H_2O nanostructures.

Density of states of the (PEO–Cu–Ag–H_2O) nanostructures as a function of energy levels was calculated by employing the DFT–B3LYP/LanL2DZ level of theory.

Figure 7 shows the degenerated states as a function of energy

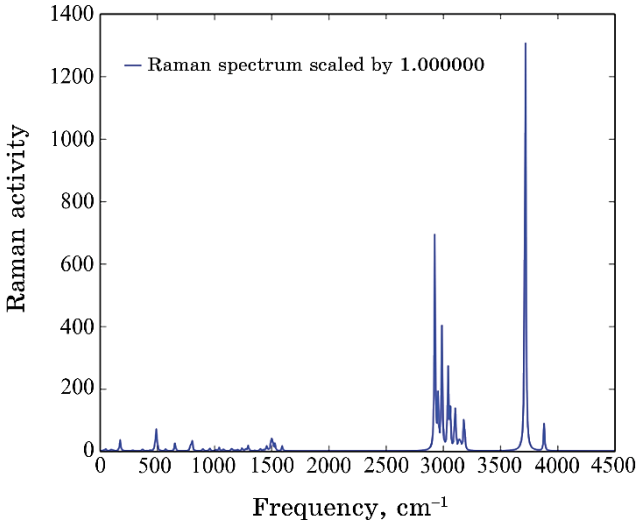

Fig. 3. Raman intensities of the (PEO–Cu–Ag–H_2O) nanostructures *versus* vibration frequency.

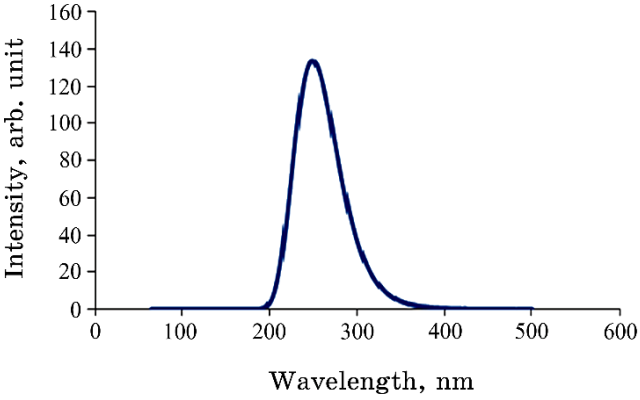

Fig. 4. UV–Vis spectrum for the (PEO–Cu–Ag–H_2O) nanostructures.

levels for the studied nanostructures. This degeneracy is caused by the existence of the new-type atoms that leads to varying the bond lengths and angles or changing the geometry of the structure.

Table 5 illustrates the thermal internal energy E_{th}, specific heat

TABLE 2. Energy gap of (PEO–Cu–Ag–H_2O) nanostructure.

PEO–Cu–Ag–H_2O nanostructures		
E_{HOMO}, eV	E_{LUMO}, eV	E_{gap}, eV
–8.293	–2.445	5.848

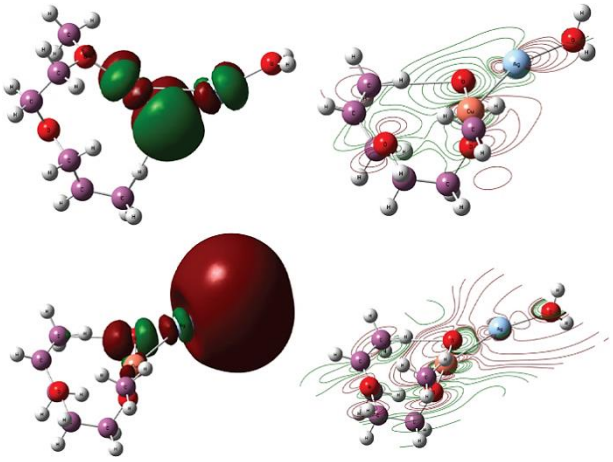

Fig. 5. The HOMO (up) and LUMO (down) distribution for the (PEO–Cu–Ag–H_2O) nanostructures.

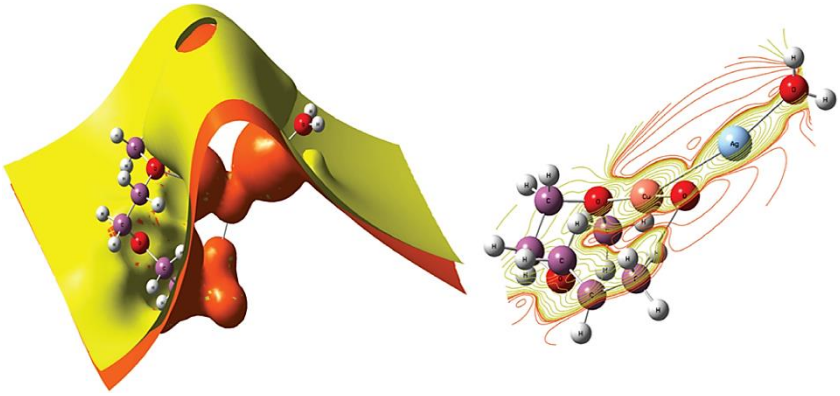

Fig. 6. Electrostatic potential surface distribution for the (PEO–Cu–Ag–H_2O) nanostructures.

TABLE 3. Electronic characteristics of (PEO–Cu–Ag–H_2O) nanostructure.

Property PEO–Cu–Ag–H_2O nanostructures	(in a.u.)
Total energy	–880.377
Ionization potential	8.293
Electron affinity	2.445
Electronegativity	5.369
Chemical hardness	2.924
Chemical softness	0.170
Chemical potential	–5.369
Electrophilicity	4.929
Dipole moment (Debye)	6.446

TABLE 4. The polarizability α_{ave} and its components for the PEO–Cu–Ag–H_2O nanostructures.

Polarizability, a.u.			
α_{xx}, a.u.	α_{yy}, a.u.	α_{zz}, a.u.	α_{ave}, a.u.
197.616	140.996	112.561	150.391

C_v and entropy S_{th} for the PEO–Cu–Ag–H_2O nanostructures calculated on the same level of theory. These properties are including all the electronic, translational, rotational, vibrational and total thermal properties.

4. CONCLUSIONS

In present work, for first time, the design of the (PEO–Cu–Ag–H_2O) nanostructures and the investigation of their structure, electronic, optical and thermal properties have been investigated to use them in solar collectors with high dispersion of metallic particles, good solar-energy absorption and high corrosion resistance. With the assistance of DFT methods, a good relaxation of the (PEO–Cu–Ag–H_2O) nanostructures is obtained. The results show that the (PEO–Cu–Ag–H_2O) nanostructures have good structure, optical, electronic and thermal properties. The results of the IR spectra calculations show that the water molecule is adsorbed on the surface of the (PEO–Cu–Ag–H_2O) nanostructure without any chemical reaction with it. The (PEO–Cu–Ag–H_2O) nanostructure has high absorption of solar energy at wavelength ranged from 200 to 350 nm. Energy gap is a useful inherent property. In hard molecule with a large energy gap, its electron density is changed more hardly than in soft

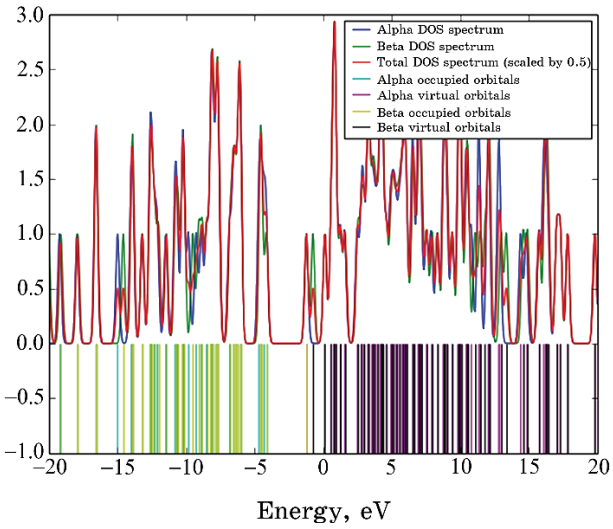

Fig. 7. DOS of (PEO–Cu–Ag–H_2O) nanostructure.

TABLE 5. E_{th}, C_v and S_{th} of the (PEO–Cu–Ag–H_2O) nanostructures.

Thermal corrections (Hartree/particle)			
	E_{th}, kCal/mole	C_v, Cal/(mole·K)	S_{th}, Cal/(mole·K)
Electronic	0.000	0.000	1.377
Translational	0.889	2.981	43.470
Rotational	0.889	2.981	33.453
Vibrational	143.890	56.661	76.733
Total	145.668	62.623	155.033

molecule. Finally, the results indicate that (PEO–Cu–Ag–H_2O) nanostructures may be use in renewable energy field for solar collectors.

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