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THE STRUCTURAL AND ELECTRONIC PROPERTIES OF n-POLYPYRROLE/ HOLLOW GOLD MONOLAYER HYBRID NANOSTRUCTURES BY AB-INITIO SIMULATIONS

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In this work, we have investigated the new generation hybrid nanostructures combined with n-Polypyrolle monomer and hollow Au monolayer surfaces by ab-inito simulation method. Interfacial interactions between n-PPy monomer and the hollow FCC Au monolayer surfaces have obtained by density functional calculations (DFT) using the GAUSSIAN 09 program package. We have considered the one and two monomer of PPy located at inner part of hollow monolayer of gold (100) surfaces. Optimized geometry, Quantum chemical calculations of hybrid nanostructures have obtained. The results show that the interface energy increases the number of PPy monomer increases. And depends on the position of the n-PPy deposited in the hollow Au (100) monolayer. It has found that the electron transfers from n-PPy to monolayer surface of the hybrid structure.

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1. Introduction

Recently, gold nanomaterials (such as nanoparticles, nanowires, nanodisks, nanolayers) have great attention due to their unique properties for the applications of catalytic, electronic and optic devices in the nanoscience field [1-3]. The physical and chemical properties of gold nanomaterials are differing from the corresponding bulk materials [2]. Gold nanomaterials due to their tunable size and shape dependent optical properties have been used in various biomedical applications and surface coatings [4-7]. Two dimension (2D) of gold nanomaterials as nanosheets or nanoplates exhibit superior properties than those of 1D and 0D ones. Self-assembly of Au NPs or clusters is another effective approach for the preparation of Au nanosheets [8].

An essential aspect of those nanomaterials is surface functionalization for multifunctional applications [4-6]. In addition to this, Gold nanomaterials in combination with conducting polymers (CPs) have been designed to use in sensing applications for environmental, medical, pharmaceutical and biological purposes [7]. PPy is one of the most studied CPs that due to its high conductivity and environmentally friendly properties. For this reason, it has been used for several organic electronic and vivo biomedical applications [6,8]. On this line, gold nanoclusters, embedded in the pre-synthesized PPy film as the sensor platform and multienzyme-antibody functionalized gold nanorods [5]. Shamaeli and Alizadeh designed a novel dual-responsive system based PPy -Functionalized Gold Nanoparticle (GNP) –nano-biocomposite (NBC) with the large specific surface for controlled loading and release of insulin [6].

Understanding the detail information about how gold atoms and ligands interact and are arranged in the hybrid nanocluster is highly crucial for future applications, including signal transmittance properties such as electron transport. The determination of those structures is challenging [9]. Because of the unusual crystal structures of gold nanomaterials [10]. Topological

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surface states of Gold are important for the studies on the polymer adsorption of gold surfaces [11]. Thus, ab -initio atomistic simulations method has used to obtain more information about such hybrid structures of polymer-gold. The formation mechanism of many 2D metal nanostructure hybrids and their structure-property relationships are heavily lacking and need to be substantially strengthened [9]. In addition to the mentioned experimental data, according to our knowledge, the functionality of gold monolayer of hollow nanosheet with PPy has been unknown. This work will contribute on to the studies of this subject.

As far as, according to our knowledge, there is no any report about the theoretical calculations of title hybrid structures by DFT based ab-inito simulations. Here, we have done some theoretical calculations (structural characteristics, quantum chemical calculations, adsorbed energy) of this hybrid nanostructure which has been studied for the first time. Here, the GAUSSIAN 09W package [12] is employed with DFT calculations for those constructed hybrid structures. Geometrically optimized structures, HOMO-LUMO energies, Mulliken charges, Molecular electrostatic potential (ESP) are presented. The thermodynamic functions for the title structures such as entropy, heat capacity and enthalpy were performed at ambient temperature and pressure.

2. Materials and method

First, we have constructed the hollow Au (100) monolayer surfaces by cutting hollow Au nanoparticle through [100] direction using OVITO program [13]. Then the one and two monomer of PPy have located at inner part of hollow Au (100) nano-surfaces in order to construct hybrid structures. The hollow Au (100) monolayer surface includes 28 Au atoms. The PPy monomer has four carbon (C) atoms, five hydrogen (H) atoms and 1 nitrogen (N) atom. Thus the first hybrid structure is about C1 point group with C4H5Au28N1 Stoichiometry. The second hybrid structure is also C1 point group with C8H10Au28N2 stoichiometry.

Here, the GAUSSIAN 09W package [12] is employed with constructed the hybrid nanostructures and DFT calculations for those constructed hybrid structures. Each monomer of n-PPy (n=1,2) and hollow Au (100) monolayer surface of hollow nanosheet and hybrid nanostructure have been fully optimized separately using the most popular Becke's three-parameter hybrid functional, B3 [12], with the non-local correlation of Lee–Yang–Parr, LYP, abbreviated as the B3LYP method without constraint. Geometric optimization adjusts geometry to decrease the total energy until it reaches the nearest minimum. Theoretically, the geometric optimizations have been done using the density functional theory (DFT) method with the lanl2dz basis set. By taking into account the interface interactions, the adsorbed energy between polymer monomers and hollow monolayer -Au surfaces were obtained from the minimized energy values by

$$E_{\text{int}} = (E_{comp} - (\text{E}_{sheet} + E_{poly}))/\text{n} \qquad 1)$$

where E_{int} is the interaction energy between n-PPy and monolayer-sheet, E_{comp} is the total energy of the n-PPy/monolayer-sheet nanocomposite, E_{sheet} is the total energy of the gold hollow nanosheet, E_{poly} is the total energy of the n-PPy and n: the number of the monomers [14,15]. The frontier molecular orbital energies were also calculated with DFT/B3LYP/LANL2DZ and spin singlet by Gaussian 09W [12]. The Highest Occupied Molecular Orbital (HOMO), the Lowest Unoccupied Molecular Orbital (LUMO) levels and the E_{HOMO}–E_{LUMO} gap are significant on the electronic properties of the structure because they are an indicator of molecular reactivity and properties. The HOMO and LUMO orbitals for molecules represent electron donor and electron acceptor abilities. The energy gap between the eigenvalues of HOMO and LUMO reflects the chemical stability of the molecule and given by $\Delta E = E_{LUMO} - E_{HOMO}$. The smaller the energy difference ΔE, the easier the interaction of the reactants and the reaction. The ionization potential energy (I) is the minimum energy required to remove an electron from the molecule in the gas

phase. The Ionization Energy is as I= $-E_{HOMO}$. Electron affinity (A) is defined as the amount of energy that is increased when an electron is added to the molecule in the gas phase. It is given by A= $-E_{LUMO.}$ Electronegativity (χ) refers to the ability of an atom in the molecule to pull electrons, as χ=(I+A)/2. Chemical hardness (η) is a measure of inhibition of charge transfer in the molecule with η=(I-A)/2. Molecules with high chemical hardness values have little or no intermolecular charge transfer. Chemical Softness can define as S=1/2η. The dipole moment is other important electronic property of materials. The bigger the dipole moment represents the stronger intermolecular interactions. The chemical potential, (μ) is defined as the negative of the value of electronegativity. The electrophilicity index (ω) denotes the capability of a material to accept electrons given by $\omega = (\mu^2/\eta)$.

3. Results and discussion

First, we have constructed the hollow Au monolayer surfaces by cutting through [100] direction of the hollow gold nanoparticle [2] with diameter of 2nm and one atom thick which includes 1nm size of a void. The number of monomers, n=1,2 the one and two monomer of PPy have located at inner part of hollow Au (100) nano-surfaces in order to understand of the properties of hybrid structures. We have selected the different combinations of the monomer of PPy at Au hollow monolayer surfaces which was considered at the minimum Energy. The optimized geometries of the selected hybrid structures with n monomers of PPy are given in Fig. 1.

A. Geometric Optimization

Optimization of PPy monomer/Au hollow monolayer hybrid structures was carried out using the different PPy monomer combinations at the edges of inner and outer part of Au hollow monolayer surfaces. All the optimized structures have computed with DFT/B3LYP/LANL2DZ basis set by Gaussian 09W. The optimized geometry of the monomer of PPy, and each Au (100) monolayer surfaces are illustrated in Fig.1.

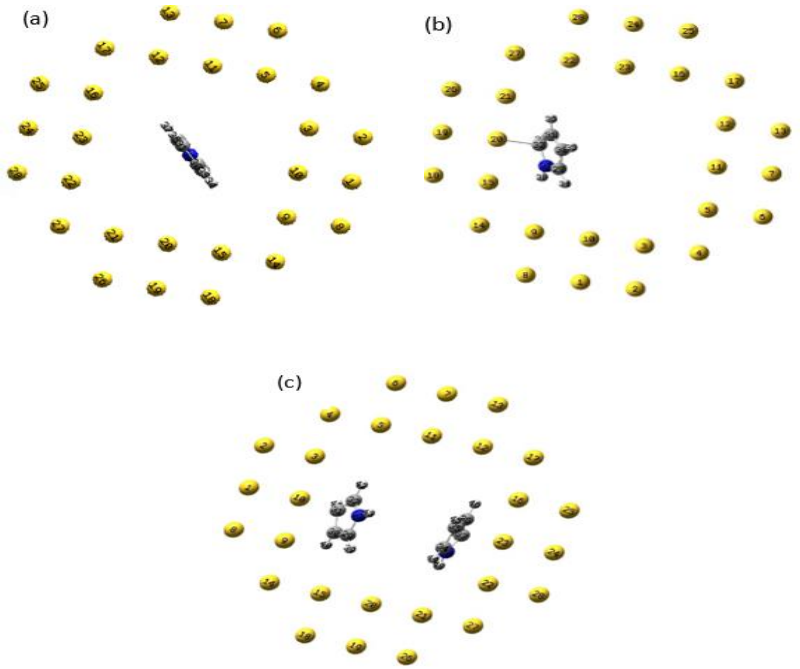

Fig. 1. Optimized geometries of title hybrid structures of PP y monomer a) centred and b) bounded at the edge of inner surfaces, both in C4H5Au28N1 stoichiometry and c) two PP y monomers by C8H10Au28N2 stoichiometry with atomic numbering

It is evident in Fig. 1b that the C32 atoms in PPy monomer has bounded with the Au20 atoms of Au (100) hollow monolayer. However, there is no bound case for the second hybrid structure of two monomers of PPy and hollow Au monolayer.

B. Mulliken Charges and Molecular Electrostatic Potential

At this level, we have computed the Muliken Charges and electrostatic potential of the title hybrid structures. All studies performed using the B3LYP-lanl2dz basis set and presented in Fig. 2.

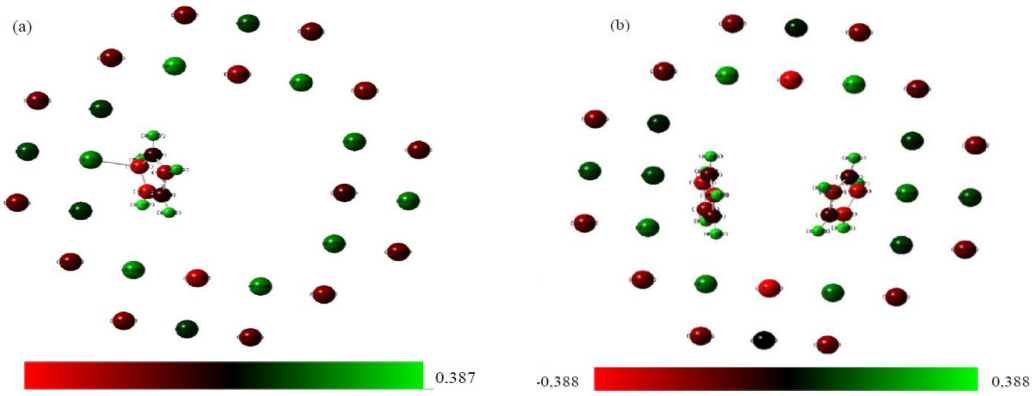

Fig. 2. Mulliken charge distribution of hybrid structures for a) PP y monomer b) two PP y monomers located at the inner edges of Au (100) hollow monolayer.

The calculation of atomic charges plays a key role in order to quantum mechanical calculations for the system. Because they affect many properties of the system such as electronic structure of the system. In Fig. 2a, the Mulliken atomic net charge value for the bounded PPy monomer is 0,525941 ē. In Fig.2b, the Mulliken net atomic charges for the left and right hand side of PPy monomers are 0.568477 ē and 0.499235 ē, respectively. The sum of Mulliken atomic charges is also equal to zero. Thus the Mulliken atomic net charge value: of hollow Au (100) monolayer surface is increased /decreased (positively/negatively) from (-0.525941ē) to (-0.533856ē) by deposition of nPPy monomers. The comparison of the natural atomic charge values, ē calculated from the Mulliken population analysis between the hollow Au (100) monolayer deposited with 1PPy (given in Fig. 1b and Fig. 2a) and without 1PPy is given in Fig. 3.

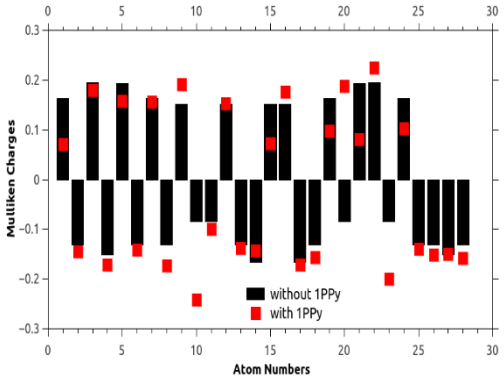

Fig. 3. Plot of natural Mulliken charges on each atom of hollow Au (100) monolayer

Table 1. Comparison of Natural atomic charges from Mulliken Population Analysis (MPA) using DFT calculations of title hybrid structures in gas phase.

Au atoms in Hollow Au(100) monolayer C1Au28					Au atoms in C8H10Au28N2 stoichiometry			
Num.	charge(ē)	**Num.**	charge(ē)		**Num.**	charge(ē)	**Num**.	charge(ē)
Au1	0,162107	**Au**15	0,150903		**Au**1	0.110668	**Au**15	0.173038
Au2	-0,131214	**Au**16	0,150877		**Au**2	-0.168466	**Au**16	0.067798
Au3	0,19385	**Au**17	-0,166186		**Au**3	0.047134	**Au**17	-0.155700
Au4	-0,151851	**Au**18	-0,13172		**Au**4	-0.159615	**Au**18	-0.182431
Au5	0,193817	**Au**19	0,162106		**Au**5	0.217673	**Au**19	-0.007987
Au6	-0,131206	**Au**20	-0,084889		**Au**6	-0.174574	**Au**20	-0.333859
Au7	0,162106	**Au**21	0,193817		**Au**7	0.041275	**Au**21	0.154146
Au8	-0,131709	**Au**22	0,193851		**Au**8	-0.169235	**Au**22	0.083842
Au9	0,150877	**Au**23	-0,084888		**Au**9	0.174532	**Au**23	0.163539
Au10	-0,084888	**Au**24	0,162106		**Au**10	0.090292	**Au**24	0.099742
Au11	-0,084888	**Au**25	-0,131711		**Au**11	-0.319348	**Au**25	-0.164421
Au12	0,150904	**Au**26	-0,131204		**Au**12	0.224275	**Au**26	-0.189750
Au13	-0,131718	**Au**27	-0,151852		**Au**13	-0.177202	**Au**27	-0.155356
Au14	-0,166186	**Au**28	-0,131212		**Au**14	-0.191819	**Au**28	-0.165906
Net Millikan atomic charges of Au atoms: 0ē					Net Milliken atomic charges of Au atoms: **(-0.533856ē)**			

It has been noted the gold atoms of Au3, Au5, Au21 and Au22 have large positive charges while Au14, Au17 have also large negative net charges in hollow Au (100) monolayer without n PPy monomer. On the other hand, the positive charges on gold atoms of Au5, Au12 have observed for the hollow Au (100) monolayer deposited with 2PPy monomers where the net Mulliken atomic charge of Au atoms is (-0.533856ē). It is obvious that the charge transfers from 2PPy monomers to hollow Au (100) monolayer is larger than that one of 1PPy.

Molecular Electrostatic Potential

At this level, we have computed the electrostatic potential of the title hybrid structures. MEP studies performed using the B3LYP-lanl2dz basis set and presented in Fig 4 for hollow monolayer of Au (100) surfaces by comparison with PPy monomers each other. Different colours on the ESP map show different values of ESP. All colours in this range from red to blue were used. Red colour is related with negative charge regions while blue one is positive charge regions. The potential increases from red to blue.

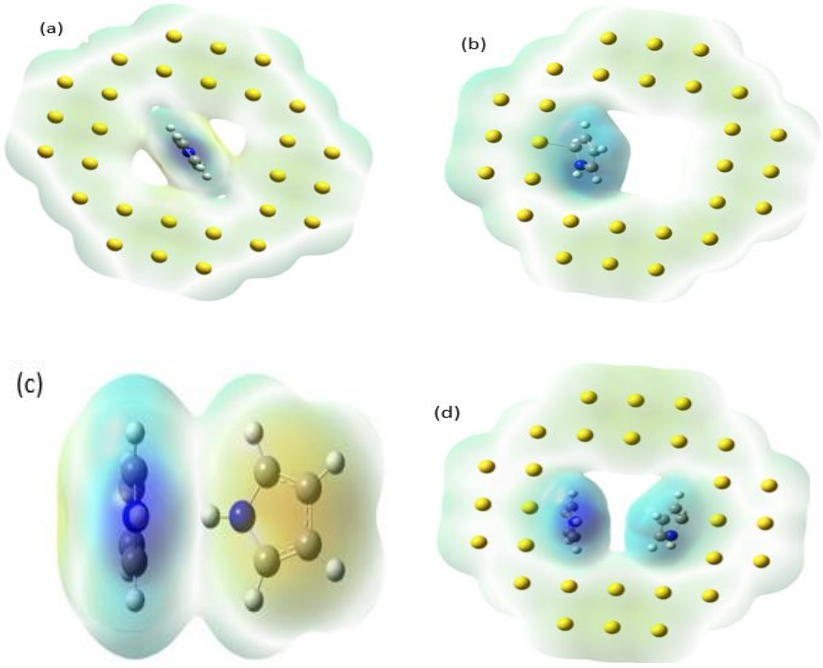

Fig. 4. Comparison of ESP for a) PP y monomer at centre and b) PP y monomer at the edge of inner part of hybrid structure c) two PP y monomers and d) two monomers at centre in hybrid structure

As seen Fig. 4c, the partially negative region can observe around the second monomer located at right hand side where a positive maximum region concentrated on the centre of first monomer placed at left hand side. In Fig. 4d, the light blue region around the H44, H45, H46 hydrogen atoms in the second monomer of left hand side indicates the slight electron definition.

C. Frontier molecule Orbital (HOMO-LUMO) Analysis

To study the electrical and optical properties of organic structures, the frontier molecule orbital analysis is very useful method. The calculated HOMO-LUMO energies, and the energy gap of $\Delta E_{HOMO-LUMO}$ are illustrated in Fig. 5 for the title hybrid structures.

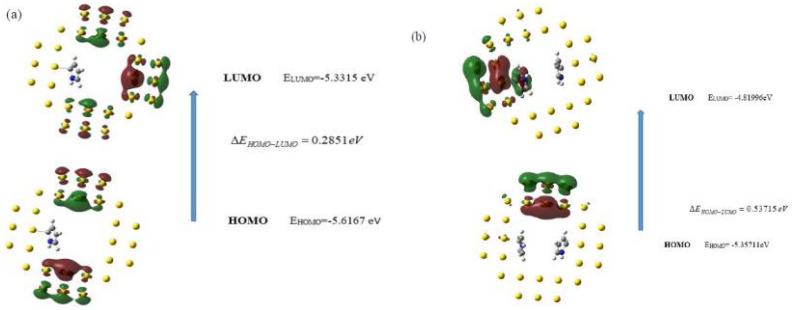

Fig. 5. HOMO-LUMO Energies for hollow Au (100) monolayer with a)1PPy and b)2PPy monomers

The occurrence of the inter-charge transformation in the molecular structure can be explored with HOMO-LUMO analysis. As seen in Fig.5 that the band gap between HOMO-LUMO increases by the number of monomers.

The physicochemical properties of each system, such as band gap between HOMO-LUMO, the ionization energy (I), electron affinity (A), electronegativity (χ), chemical hardness (η)

and softness (S) have been calculated using HOMO_LUMO energies of (100) surface of Au monolayer of hollow nanosheet, Au (100), the monomer of PPy (1PPy) and hybrid structure. By comparison with each other, the calculated values are given in Table 2. The interface energy between the hollow Au (100) monolayer with n(PPy) monomers are calculated by Eq. 1 and given in Table 3.

Table 2. Physicochemical properties of the title hybrid structures

Properties	Hybrid Structures of C4H5Au28N1		Hybrid Structure of C8H10Au28N2
	1PPy (centred)	1PPy (at edge)	2PPy
LUMO (eV)	-5.51031	-5.33153	-4.81996
HOMO (eV)	-5.77018	-5.61670	-5.35711
Energy Gap ΔE_{HL} (eV)	0.25987	0,28517	0.53715
Ionization Energy (I) (eV)	5.77018	5.61670	5.35711
Electron Affinity (A) (eV)	5.51031	5.33153	4.81996
Electro negativity (χ) (eV)	5.640245	5.474115	5.08854
Hardness (η) (eV)	0.129935	0.142585	0.268575
Softness (S) (eV^{-1})	3.84808	3.50668	1.861677

The electronegativity (χ) values of the title hybrid structures in Table 2 can be seen as the energy decrease when a very small amount of electronic charge added to the system. The chemical potential (μ) defines as ($-\chi$). The μ values of the title hybrid systems given in Table 2 are 5.640245, 5,474115, and 5,08854, respectively. The electrophilicity index (ω) of the studied hybrid structures from left to right hand side given in Table 2 are 0.25987, 0,28517 and 0,53715, respectively.

Table 3. Energy values at the interface of n PP y monomer and Au (100) hollow monolayer surfaces.

	Hybrid Structures of C4H5Au28N1		Hybrid Structure of C8H10Au28N2
Energy	1PPy (centred)	1PPy (at edge)	2PPy
E_{poly} (a. u)	-210.13859995	-210.13859995	-420.28368110
E_{sheet} (a. u)	-3793.62389687	-3793.62389687	-3793.62389687
E_{comp} (a. u)	-4003.76524458	-4003.79717902	-4213.96476848
E_{int} (a. u)	-0.00274776	-0.0346822	-0.028595255
E_{int} (eV)	-0.0747703937	-0.9437511824	-0.7781168933

As seen in Table 3, the position of PPy deeply influenced the interfacial interaction. It is beneficial to understanding the interfacial interaction between nPPy and hollow Au (100) monolayer. Among the title hybrid structures, the Py monomer located at edge of left hand side of inner part interacts strongly with hollow Au (100) monolayer surface. That is guiding the fabrication of the polymer/ Au (100) hollow monolayer nanocomposites. The calculated energy values are compatible each other and in good agreement with those obtained by experiment in literature [16]

D. Thermodynamic Properties

The total thermal energy and the standard thermodynamic functions such as entropy (S), heat capacity (Cp) and enthalpy (H) of the title structures were obtained at 298.15K and 1atm pressure by using basis of B3LYP/ lanl2dz level and results listed in Table 4. All these parameters will be helpful information about further study of the title structures. It has observed that the dipole moment values of title structures from left to right in Table4 are 1,3349 Debye, 7.9131 Debye and 3.6254Debye, respectively. It has noted that the bounded PPy has the highest dipole moment value which is in a good agreement with experiments. [16] and other calculations [17].

It is clear in Table 4 that the entropy value increases by the number of monomers. It is pointed that the equilibrium of the hybrid system is increasing with nPPy.

Table 4. The calculated thermodynamic parameters of PP y /Hollow Au (100) monolayer hybrid structures at 298.15K and 1 atm. pressure.

Parameter	Hybrid Structures of C4H5Au28N1		Hybrid Structure of C8H10Au28N2
	1PPy (centred)	1PPy (at edge)	2PPy
Zero point vibrational energy (Kcal /mole)	52.33707	53.12860	106.33878
Entropy (Cal /mole K)			
Total	129.273	120.637	153.309
Translational	51.707	51.707	51.743
Rotational	48.115	48.120	48.129
Vibrational	29.450	20.809	53.438
C_v (Cal /mole K)			
Total	22.244	23.350	44.940
Translational	2.981	2.981	2.981
Rotational	2.981	2.981	2.981
Vibrational	16.283	17.388	38.978
Energy(Thermal) (Kcal /mole)			
Total	57.003	57.703	114.872
Translational	0.889	0.889	0.889
Rotational	0.889	0.889	0.889
Vibrational	55.226	55.925	113.095

4. Conclusions

In this work, we have investigated the interfacial interaction between Au (100) surface monolayer of hollow nanosheet and PPy as a hybrid structure by using Gaussian 09W DFT/B3LYP/LANL2DZ/spin singlet calculations. We have calculated the physicochemical, electronic and thermodynamic properties of title hybrid structure. We have found that the Py monomer, which is placed at the inner edge of Au (100) monolayer of hollow nanosheet causes more changes in the HOMO-LUMO energy values of the Au (100) monolayer surface than that of the centred one. Thus, there are strong interactions between the gold nanosheet and n-pyrrole monomer. The small dipole moment represents that there are the smallest intermolecular interactions between n-PPy and hollow monolayer of gold (100) surface. The energy gap between HOMO and LUMO energies of the constructed hybrid structure show that Py centered of Au (100) monolayer surface of hollow nanosheet is a good architecture with exceptional stability. By comparison between the ionization energies of Au monolayer of hollow nanosheet and Au/PPy hybrid nanocomposite, it is seen that the minimum energy required to remove an electron from the molecule is even lower in the nanocomposite material. The conductivity increases and the electronegativity is reduced for the hybrid structures by the number of monomer, n. Our results are compatible with each other. As a result, Au/PPy nanocomposites incredibly versatile materials for next-generation applications. The different shape and conducting polymer can be used for constructing the hybrid structures of 2D metal nanomaterials. This work will progress on this line.

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