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Adsorption of pyrrole on $Al_{12}N_{12}$, $Al_{12}P_{12}$, $B_{12}N_{12}$, and $B_{12}P_{12}$ fullerene-like nano-cages; a first principles study

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Adsorption of pyrrole on the surfaces of four $X_{12}Y_{12}$ semiconductors ($Al_{12}N_{12}$, $Al_{12}P_{12}$, $B_{12}N_{12}$, and $B_{12}P_{12}$) is studied through density functional theory (DFT) calculations at B3LYP/6-31G(d,p) level of theory. The highest interaction energy is calculated for the adsorption of pyrrole on the surface of $Al_{12}N_{12}$ nano-cage. The adsorption energies of pyrrole on $Al_{12}N_{12}$, $Al_{12}P_{12}$, $B_{12}N_{12}$, and $B_{12}P_{12}$ are −64.6, −42.6, −12.0, −9.2 kJ mol^{-1}, respectively. Pyrrole acts as an electron donor and adsorbs at the electrophilic site of nano-cage. Charge transfer to aluminum nano-cages is higher than to boron nano-cages. Changes in electronic properties such as band gap, Fermi level, and densities of states are also analyzed in order to better understand the sensing abilities of nano-cages for pyrrole molecule. Band gaps of aluminum nano-cages ($Al_{12}N_{12}$ and $Al_{12}P_{12}$) are unaffected by adsorption of pyrrole because of comparable effect on HOMOs and LUMOs. On the other hand, band gaps of boron nano-cages are significantly reduced on adsorption of pyrrole. Boron nano-cages are better sensor for pyrrole molecule despite their lower binding energies.

1. Introduction

An important challenge in current semiconductor technology is to understand important parameters that influence the interaction of organic molecules with different semiconductors [1,2]. A few reports exist in the literature where adsorption of small organic molecules such as cyclopentene, benzene and pyrrole is demonstrated on the surface of semiconductor materials [3–5].

Pyrrole (C_4H_4NH) is colorless, volatile, nitrogen containing heterocyclic compound (see Fig. 1). Pyrrole is an aromatic compound and it exhibits chemical reactivity very similar to benzene. For example, pyrrole resists to hydrogenation and Diels-Alder reactions. However, the electron density in pyrrole is greater than that of benzene; therefore, pyrrole is categorized as p-electron excessive aromatic molecule [6].

Pyrrole has noxious impact on metal catalysts utilized in petrochemical industry therefore removal of pyrrole from crude petroleum is very important. A number of studies demonstrate the adsorption of pyrrole on different surface [7–9]. For example, Qiao et al. [7] studied the adsorption and thermal reaction of pyrrole on Si(1 0 0) through X-ray and ultra-violet photoelectron spectroscopy. Bruhn et al. [8] studied the adsorption mechanism of pyrrole on As-rich GaAs(001)-*c*(4 × 4) surface. Noei et al. [9] examined the electrical sensitivity of boron nitride nanotube toward pyrrole through DFT calculations.

Recently, nanostructure semiconductors have gained significant interest from the scientific community because of their distinct physical and chemical properties [10–12]. Particularly, group III–V semiconductors have been used in fast microelectronic devices and light-emitting diodes [13–15]. Group III–V sheets such as AlN sheets have been studied experimentally on Ag(111) support [16], and also theoretically for defects [17]. Moreover, hexagonal BN sheets are also studied as sensor [18]. Group III–V semiconductors have also been used as adsorbent and sensor for different analytes. Design of these new solid-state adsorbents/sensors is based on the high electrophilicity of III–V semiconductors. Electronic structure of these semiconductors changes on interaction with analytes. The small size of solid-state chemical adsorbents, easy synthesis, low cost and their reproducibility make them fascinating candidates for sensor applications [19].

Molecular simulation of different X_nY_n semiconductors ($X = B$, Al, … and $Y = N$, P, …) showed that the fullerene-like $X_{12}Y_{12}$ cages are the most stable ones [20,21]. $Al_{12}N_{12}$, $Al_{12}P_{12}$, $B_{12}N_{12}$ and $B_{12}P_{12}$ are four important fullerene-like nano-cages because of their

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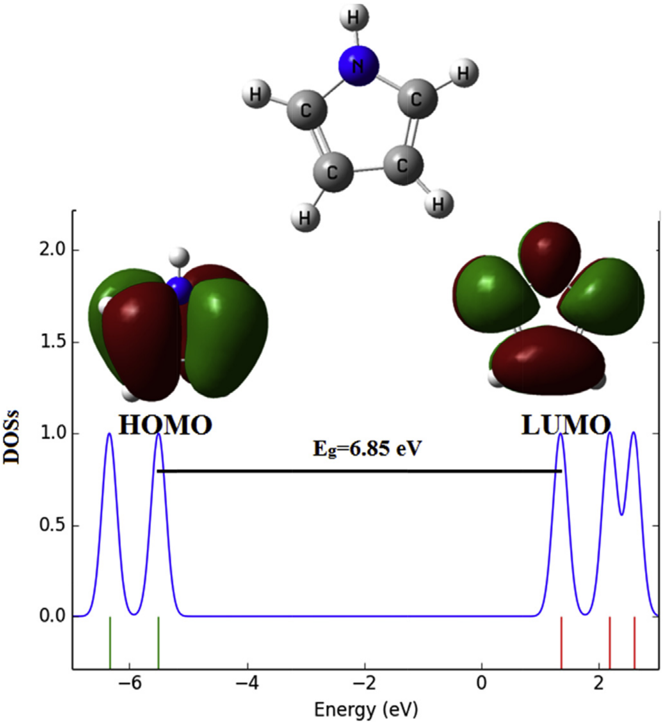

Fig. 1. The Scheme of pyrrole molecule along with its DOSs and HOMO-LUMO distribution.

particular stability, large band (HOMO-LUMO) gap, and excellent physical and chemical properties. Accordingly, these nano-cages have been overwhelmingly investigated as sensors [22–24]. Adsorption properties of a variety of analytes on the surfaces of $Al_{12}N_{12}$, $Al_{12}P_{12}$, $B_{12}N_{12}$, and $B_{12}P_{12}$ [25–28] have been demonstrated in the literature.

For example, we explored the adsorption property of guanine molecule on the surface of the above mentioned nano-cages using DFT calculations [25]. Although adsorption of guanine on $Al_{12}N_{12}$ has the highest adsorption energy; however, $B_{12}N_{12}$ and $B_{12}P_{12}$ show more changes in electronic property upon adsorption of guanine. Moreover, adsorption of nickel on the surface of $Al_{12}P_{12}$ [26] and $Al_{12}N_{12}$ [27] are also studied. The nickel atom was shown to adsorb on $Al_{12}P_{12}$ and $Al_{12}N_{12}$ in four distinct adsorption sties (four distinct geometries). Beheshtian et al. studied the interaction of CO on $B_{12}N_{12}$ nano-cage [28]. Soltani et al. [29] studied the interaction of phenol with diverse nano-cages through DFT calculations.

In the present study, we theoretically investigate the potential of four fullerene-like $X_{12}Y_{12}$ nano-cages (X = Al, B, and Y = N, P) as adsorbent for pyrrole. Based on our knowledge, the adsorption of pyrrole molecule has not been studied on the surface of above-mentioned nano-cages. The adsorption of pyrrole on the surface of nano-cages is studied through geometric, energetic and electronic analysis. For this purpose, binding energies, charge transfer, distribution of HOMO and LUMO, band gaps and densities of states are analyzed for free $X_{12}Y_{12}$ and $X_{12}Y_{12}$-P complexes.

2. Computational methods

All calculations were performed at B3LYP/6-31G(d,p) level of DFT, as implemented in Gaussian 09 suite of program [33]. The B3LYP is a reliable method for the study of geometric and electronic properties of nano-cages [27–32]. It has been previously shown that B3LYP/6-31G(d,p) is an optimal level of theory to deliver reliable and accurate results at minimum cost for a variety of systems [34–39]. Moreover, the theoretical studies on adsorption and sensor properties of nano-cages are exclusively studied at B3LYP/6-31G(d,p). Therefore, the results obtained here can be compared directly with the literature. Geometries of pyrrole-$X_{12}Y_{12}$ complexes are optimized without an symmetry constraints at B3LYP/6-31G(d,p) level of theory. The default grid for optimization in G09 is fine. The maximum force and RMS forces are 3×10^{-4} and 4.5×10^{-4} (Hartrees/Bohr and Hartrees/Radian) whereas maximum displacement and RMS displacement are 1.8×10^{-3} and 1.2×10^{-3}.

The binding energy (E_b) of pyrrole on nano-cages is defined as:

$$Eb = E(X_{12}Y_{12} - \text{pyrrole}) - E(X_{12}Y_{12}) - E(\text{pyrrole}) \qquad (1)$$

where $E(X_{12}Y_{12}$-pyrrole) is the total energy of pyrrole-$X_{12}Y_{12}$ complex, and $E(X_{12}Y_{12})$ and E(pyrrole) are the total energies of the free $X_{12}Y_{12}$ and free pyrrole molecule, respectively. The charge transfer is calculated through Mullikan and Natural Bonding Orbitals (NBO) schemes. The changes in electronic structures of nano-cages are evaluated through Frontier Molecular Orbitals (FMO), B and gap (Eg), Fermi levels and density of states. Electronic properties are also calculated at above mentioned level of theory (B3LYP/6-31G(d,p)).

3. Results and discussion

The relaxed structure of pure $Al_{12}N_{12}$, $Al_{12}P_{12}$, $B_{12}N_{12}$ and $B_{12}P_{12}$ semiconductors are well discussed in our recent paper [25] therefore, the discussion in this manuscript is restricted to changes observed on complexation with pyrrole. The pyrrole molecule is placed on $X_{12}Y_{12}$ nano-cages in two possible orientations on the semiconductor; (a) pyrrole interacts with the nano-cage through nitrogen atom(N-side), (b) π stacking where aromatic ring of pyrrole interacts with the nano-cage. Both geometries are allowed to relax during optimization in order to find the most stable structure. For all systems, relaxed structuresin side and top views are given in Fig. 2. The binding energies of pyrrole (Table 1) adsorption on $Al_{12}N_{12}$, $Al_{12}P_{12}$, $B_{12}N_{12}$ and $B_{12}P_{12}$are −64.6, −42.6, −12.0, −9.2 kJmol^{-1}, respectively. The $X_{12}Y_{12}$ ––– Pyrrole distances in $Al_{12}N_{12}$-P, $Al_{12}P_{12}$-P, $B_{12}N_{12}$-P and $B_{12}P_{12}$-P are 2.13 Å, 2.20 Å, 2.39 Å and 3.56 Å, respectively. The high bind energies of pyrrole on the surface of aluminum nano-cages suggest chemisorption of pyrrole. On the other hand, low binding energies of pyrrole on the surface of boron nano-cages suggest physisorption. Strong adsorption of pyrrole on aluminum nano-cages relates to the higher charge density on aluminum compared to boron (vide infra, charge analysis). The binding energy is inversely proportional to $X_{12}Y_{12}$ ––– Pyrrole distance. The binding energies data suggest that aluminum containing nano-cages are good adsorbent for pyrrole. Calculated binding distances for adsorption of pyrrole on the surface of $Al_{12}N_{12}$ and $Al_{12}P_{12}$ are very close to the value of 1.95 Å and 2.01 Å for adsorption of guanine on the same surfaces [25].

The binding energies of pyrrole on nitrogen containing nano-cages are higher than their phosphorus counterparts which can be attributed to higher charge density on group III atom, and hydrogen bonding interaction in nitrogen nano-cages. Al and B atoms in nitrogen containing semiconductors are more electron deficient than those in phosphorus nano-cages. The higher charge density on Al and B in nitrogen containing semiconductor render them more susceptible to nucleophilic attack of pyrrole therefore, these complexes are categorized as p-type semiconductors.

The results of charge analysis show transfer of charge from pyrrole to semiconductor (see Table 1). The nitrogen atom in