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Effects of Cl_2 adsorption over the optical and electronic properties of $Al_{12}N_{12}$ and $Al_{12}CN_{11}$ fullerenes: Density functional theory study

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ABSTRACT

Using the density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations, we studied the adsorption and dissociation of Cl_2 molecule over $Al_{12}N_{12}$ and $Al_{12}CN_{11}$ fullerenes at the room temperature. Chemisorption of Cl_2 on the $Al_{12}CN_{11}$ (−4.41 eV) is much stronger in comparison with the $Al_{12}N_{12}$ fullerene (−2.92 eV). In the most stable states, we found that the gap energy of $Al_{12}N_{12}$ is significantly altered (ΔE_g = 79%) upon the adsorption of Cl_2 compared with $Al_{12}CN_{11}$ fullerene (ΔE_g = 43%). UV–vis spectra analysis represents that the values of λ_{max} are in the red region for the adsorption structures of Cl_2 onto the pure and $Al_{12}CN_{11}$ fullerenes. We hope that our present theoretical studies can provide helpful information for further theoretical and experimental studies in the removal of this toxic gas by means of UV–vis and IR spectra.

1. Introduction

Chlorine, Cl_2, is a toxic greenish-yellow gaseous (occupational exposure limit (OEL) = 0.5 ppm) which is extensively applied for various industries related to plastics, paper products, dyestuffs, agrochemicals, pharmaceuticals, water purification and household cleaning products etc. Despite the useful various uses of chlorine, it has many harmful effects on human body like skin irritation, suffocation, sensory irritation, bronchospasm etc; and that is why there is an increasing demand of Cl_2 sensors because of increasing concern over the safety and health hazards related to this gas [1–4]. Nowadays room temperature ppb level Cl_2 sensing has been reported by using sulphonated copper phthalocyanine film with higher response and faster sensing characteristics as compared to the Sb-doped SnO_2 nano-porous films, FEP/polyaniline films and etc [5]. Altindal et al. have studied Cl_2 sensing properties of crosswise-substituted phthalocyanines as a function of temperature (5–75 °C) in the concentration ranging from 50 to 150 ppb [6]. Beheshtian and his team have shown that the Cl_2 molecule is strongly adsorbed on the ZnO nano-cluster via two mechanisms including chemisorption and dissociation with Gibbs free energy changes in the range of 0.36 to −0.92 eV at 298 K and 1 atm [7]. Nowadays, $Al_{12}N_{12}$ fullerene-like structures and nanotubes constructed of other elements have drawn considerable attention owing to their specific physical and chemical properties [8–12]. Particularly, fullerene-like nano-cages of group 3–5 elements in the periodic table have been theoretically identified and experimentally synthesized [13–19]. Especially the group III nitrides have been found as important source of nanoscale materials because of their direct bond gaps affording optical and electro-optical properties and among these, AlN nanostructures had drawn considerable attention on the basis of *ab initio* calculation which shown in the large (AlN)n (n = 2–41) family, the $Al_{12}N_{12}$ nanocages are the most stable nanostructures energetically and thus it can be as an excellent candidate inorganic fullerene [20,21]. Many studies have been shown that the $Al_{12}N_{12}$ nano-cage may be used in the potential applications of hydrogen storage and gas sensor [12,22]. Jiao and co-workers recently studied the adsorption behavior of CO_2 and N_2 molecules over AlN single-walled nanotubes at the LDA and PW91 levels in a double numerical plus polarization basis set (DNP) [23]. They found that the tube diameter have a key effect on the chemisorption of CO_2 respect to N_2 molecule. Niu and co-workers introduced that the $Al_{12}N_{12}$ nano-cage by doping the alkali metal atom (Li, Na, and K) which can effectively reduce the energy gap values respect to the pure $Al_{12}N_{12}$ nano-cage [24]. Wang and co-workers reported potential of AlN nanostructures as hydrogen storage materials, while the binding of one H_2 molecule is in the value of 0.1–0.2 eV which this binding leads to 4.7 wt % hydrogen storage [25]. Baei and co-authors have analyzed the OCN^- chemisorption over AlN nanostructures by DFT simulation [26]. Soltani and co-workers have investigated the adsorption behavior of NO_2 and SO_2 molecules over $Al_{12}N_{12}$ nano-cage sensitized with gallium and magnesium using DFT calculations. They found that the Mg-doped $Al_{11}N_{12}$ nano-cage has high sensitivity to NO_2 and SO_2 molecules than Ga-doped $Al_{11}N_{12}$ nano-cage [27]. Recently, chigo Anota and co-workers have studied the adsorption, activation and possible dissociation of the glucose molecule on the magnetic $[BN\ fullerene\text{-}B_6]^-$ system

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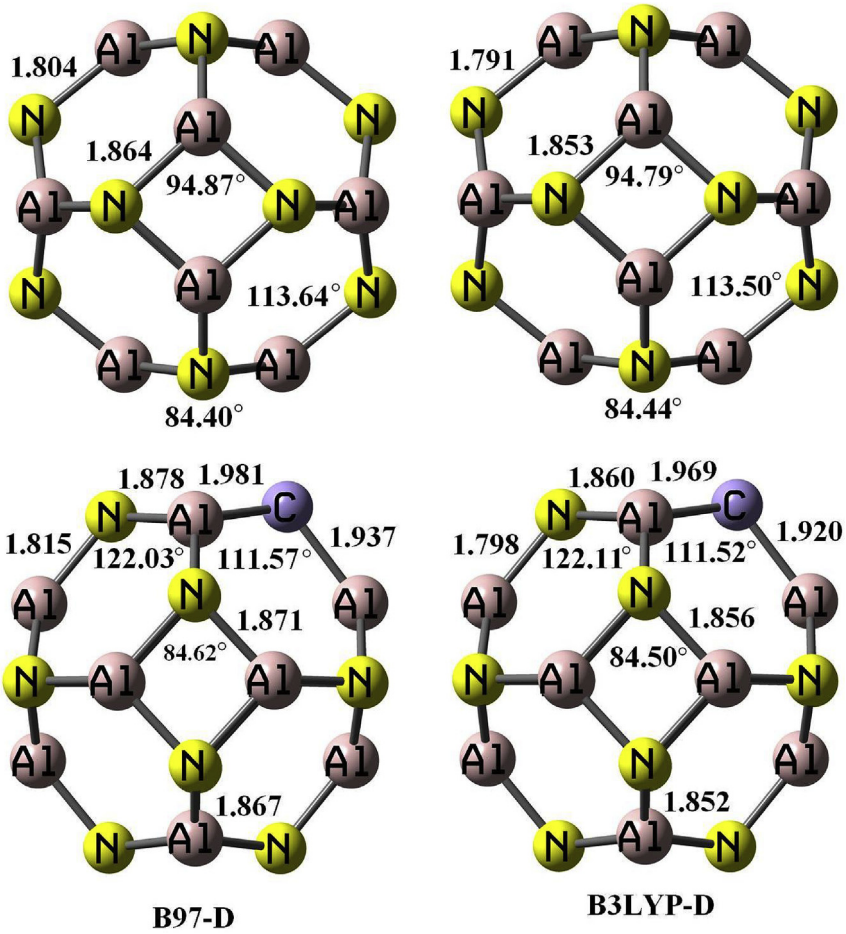

Fig. 1. Optimized structures of the $Al_{12}N_{12}$ and $Al_{12}CN_{11}$ fullerenes.

by means of density functional theory calculations [28].

In this work, we have taken the pure and $Al_{12}CN_{11}$ nano-cages as an efficient catalyst to remove of Cl_2 and we evaluated the impact of adsorption on the structural, electronic, optical properties of the fullerenes.

2. Computational methods

Geometry relaxations and total density of states (TDOS) analysis of the Cl_2, $Al_{12}N_{12}$ and $Al_{12}CN_{11}$ fullerenes are performed with a DFT-B3LYP method augmented with an empirical dispersion term (B3LYP-D) [29,30] and then compared to B97 hybrid density functional accompanied by a dispersion-corrected GGA, B97-D [31]. All the geometrical relaxations and binding energies computations has been carried out using GAMESS suite of program [32] at the density functional theory (DFT) level using B3LYP-D/6–311 + + G** and B97-D/6–311 + + G** methods. The B3LYP-D and B97-D functionals of density functional theory have been considered by us and others to study the adsorption behavior and interaction details of gas molecules with the different nanostructures [33–36]. The basis set superposition error (BSSE) for the adsorption energy was corrected by using implementing the counterpoise method. The UV–vis absorption spectrum of Cl_2 adsorbed over the $Al_{12}N_{12}$ and $Al_{12}CN_{11}$ surfaces have been carried out by means of time-dependent density functional theory (TD-DFT) calculations at the CAM-B3LYP functional and 6–311 + + G** basis set. We have determined the adsorption energy (E_{ad}) of Cl_2 on the pure and $Al_{12}CN_{11}$ fullerenes as follows:

$$E_{ad} = E_{Al12N12-Cl2} - (E_{Al12N12} + E_{Cl2}) + E_{BSSE} \quad (1)$$

$$E_{ad} = E_{Al12CN11-Cl2} - (E_{Al12CN11} + E_{Cl2}) + E_{BSSE} \quad (2)$$

where $E_{Al12N12-Cl2}$ and $E_{Al12CN11-Cl2}$ are the total energies of $Al_{12}N_{12}$ and $Al_{12}CN_{11}$ fullerenes interacting with Cl_2. $E_{Al12N12}$ and $E_{Al12CN11}$ are total energies of the pure $Al_{12}N_{12}$ and $Al_{12}CN_{11}$ fullerenes. E_{Cl2} is the total energy of Cl_2 molecule. Natural bond orbital (NBO) analysis, molecular electrostatic potential (MEP), and total density of states (TDOS) analyses were calculated by using B3LYP method with 6–311 + + G** basis set.

3. Results and discussion

3.1. The Cl_2 adsorbed on $Al_{12}N_{12}$ and $Al_{12}CN_{11}$ fullerenes

Fig. 1 presents the relaxed structures of $Al_{12}N_{12}$ and $Al_{12}CN_{11}$ fullerenes that are made from 6 squares and 8 hexagons according to B3LYP-D and B97-D methods. NBO analysis demonstrates that the charge point value for Al and N atoms of $Al_{12}N_{12}$ are +0.109 and −0.109 e by B3LYP-D functional and +0.947 and −0.947 e by B97-D functional, respectively, while after doping process in the nano-cluster, the value of point charges for Al, C, and N atoms are found about +0.343, −0.433, and −0.169 e by B3LYP-D functional and +0.918, −0.857, and −0.947 e by B97-D functional, respectively. Based on natural bond orbital (NBO) analysis, the positive and negative charges upon Al and N atoms of $Al_{12}N_{12}$ fullerene is found to be +1.823 and −1.823 e, respectively, which are consistent with those reported by