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A DFT study on the formaldehyde (H_2CO and $(H_2CO)_2$) monitoring using pristine $B_{12}N_{12}$ nanocluster

Ehsan Shakerzadeh

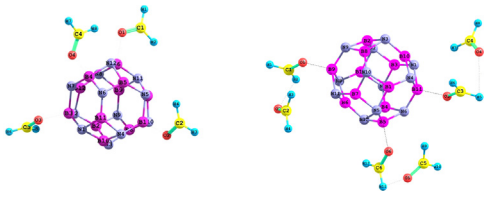
Chemistry Department, Faculty of Science, Shahid Chamran University, Ahvaz, Iran

HIGHLIGHTS

- The interactions between H_2CO and $(H_2CO)_2$ with $B_{12}N_{12}$ investigated using DFT.
- $B_{12}N_{12}$ Could adsorb up to four formaldehyde monomer molecules.
- $B_{12}N_{12}$ Could adsorb up to three formaldehyde dimer.
- Formaldehyde adsorption dramatically change electric properties.
- $B_{12}N_{12}$ would be a highly sensitive formaldehyde chemical sensor.

GRAPHICAL ABSTRACT

The pristine $B_{12}N_{12}$ nanocluster effectively interacted with formaldehyde (H_2CO and $(H_2CO)_2$) and could be a promising formaldehyde chemical sensor.



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ABSTRACT

The interaction between formaldehyde monomer (H_2CO) as well as dimer ($(H_2CO)_2$) and pristine $B_{12}N_{12}$ nanocluster is investigated at B3LYP/6-311++G(d,p) level of theory. It is found that in contrary to the pristine boron nitride nanotube and nanosheet, formaldehyde adsorption induce considerable variation in the electronic properties of the $B_{12}N_{12}$ nanocluster. Also it is shown that the pristine $B_{12}N_{12}$ cluster could adsorb up to four monomer and three dimer of formaldehyde molecules in which the HOMO–LUMO gap decreased about 38–55%. Since the conductivity of the $B_{12}N_{12}$ nanocluster changes by the adsorption of formaldehyde molecules, the presence of this toxic gas could be detected. The Bader theory of atoms in molecules (AIM) is also applied to analyze the interaction of formaldehyde with nanocluster. It is suggested pristine $B_{12}N_{12}$ nanocluster could be a promising candidate for detecting formaldehyde molecule. The results indicate that $B_{12}N_{12}$ may be a promising chemical sensor for detection of formaldehyde molecule.

1. Introduction

Boron nitride nanomaterials, including nanotubes, nanocapsules, nanosheets and nanoclusters exhibit different desirable physical and chemical properties in comparison to their carbon counterparts. They are electrically insulator with a wide band gap (~4.00–6.00 eV) and show high thermal conductivity together with inherent noncytotoxicity [1]. These unique and important properties cause that boron nitride nanostructures display great potential in many fields, especially in the nanodevices such as transistors and chemical sensors. Recently, several studies on boron nitride fullerene materials have been also reported due to their exotic properties [2–4]. The geometries and stability of fullerene-like $(BN)_n$ nanoclusters have been theoretically investigated by many researchers [5–9]. Fowler et. al [5] theoretically showed that the $B_{12}N_{12}$, $B_{16}N_{16}$ and $B_{28}N_{28}$ are magic stable BN fullerenes and $B_{12}N_{12}$ cluster is the more stable one among them. Theoretical studies demonstrated that the $B_{12}N_{12}$ cluster built from square and hexagonal rings, is more stable than one built from pentagons and hexagons. Eventually Oku et al. [10] have synthesized the $B_{12}N_{12}$ cluster, detected by laser desorption time-offlight mass spectrometry. They confirmed that $B_{12}N_{12}$ cluster is semiconductor in which consist of square and hexagonal rings.

E-mail address: e.shakerzadeh@scu.ac.ir

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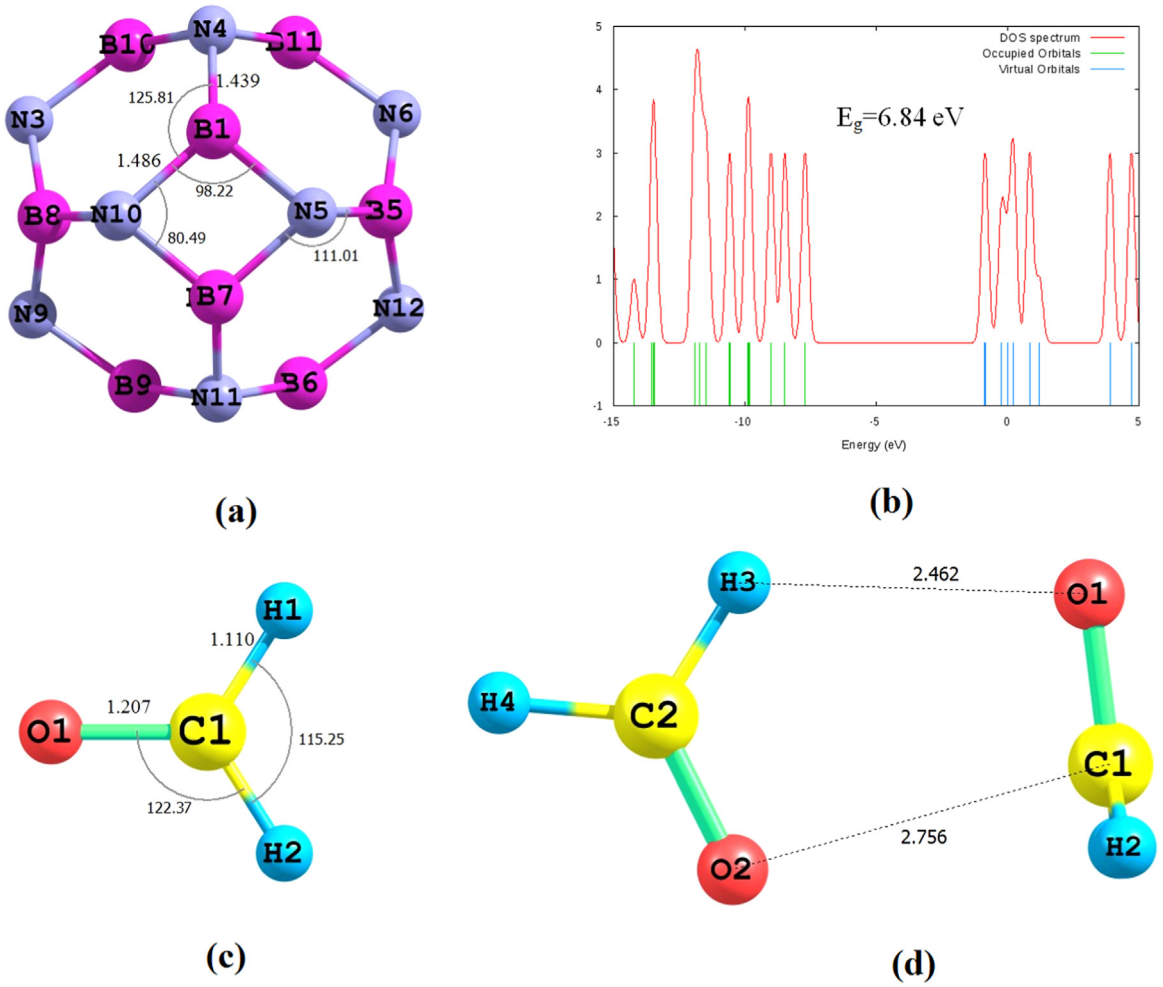

Fig. 1. (a) The optimized geometry, (b) electronic density of states (DOS) spectrum of the pristine $B_{12}N_{12}$ nanocluster as well as the optimized geometry of (c) H_2CO and (d) $(H_2CO)_2$ molecules.

Undoubtedly formaldehyde (H_2CO) is one of the most common and the well-known indoor air pollutant due to its widely applications in some constructive and decorative materials [11,12]. Notice that formaldehyde could be considered as $(H_2CO)_2$ dimer. It is the most abundant carbonyl chemicals which are well-known to cause headache, nausea, childhood asthma, pulmonary edema, nasal tumor and irritation of skin [13–16]. Discussion about formaldehyde as a possible carcinogen is also reported [17,18]. Therefore Monitoring and controlling its exposure in both residential and industrial environments are very important. Many efforts have been made to find fast, sensitive and simple methods for detecting formaldehyde such as polarography, gas chromatography and fluorometry [19,20]. However, these methods are not sensitive enough and require expensive instruments, have high detection limits or require long sampling intervals. Hence there is an increasing demand for finding fast and simple formaldehyde monitoring methods, and this has stimulated research activities in the field of sensor technology [21]. Lately, several theoretical studies are performed to introduce different materials for detecting H_2CO monomer molecule such as to Al-doped graphene [22], TiO_2 surface [23], boron-doped CNTs [24], silicon-doped BNNT [25], silicon carbide nanotube [26], nitrogen vacancy defected boron nitride nanosheet [27] and vacancy defected graphene doped with B, N, and S [28].

The previous studies indicated that pristine boron nitride nanotube and nanosheet fail to detect the presence of formaldehyde [25,27]. Therefore different modifications such as defect and dopant are necessary to activate the surface of these nanostructures for adsorbing the H_2CO molecule. Recently the interaction of pristine $B_{12}N_{12}$ nanocluster with different molecules such as CO [29], CO_2 [30], NO_2 [31] NO, H_2, N_2 and CH_4 [32] are investigated through density functional theory. In this study DFT calculations have been performed to scrutinize the adsorption of formaldehyde onto pristine $B_{12}N_{12}$ nanocluster without manipulating its structure. The purpose of this work is to exploit the potential application of boron nitride-based gas sensor. The obtained results may provide a new insight to the gas sensor nanotechnology.

2. Computational details

The geometries of all considered structures are fully optimized at B3LYP/6-311++G(d,p) level of theory and the nature of the stationary points are checked by frequency analysis at the same computational level of theory. It is noteworthy that the B3LYP approach is conventional approach for studying nanostructures [32]. All calculations are performed using Gaussian 03 package [33]. The Atoms in molecules (AIM) theory has been used to better understand the adsorption and the nature of the interaction of the gases on $B_{12}N_{12}$ nanocluster. In the AIM analyses, existence of an interaction is indicated by the presence of a bond critical point (BCP) and the strength of the bond is estimated from the magnitude of the electron density at the bond critical point (ρ_{BCP}).