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A DFT Study of H_2 Molecule Adsorption at the Fullerene-Like Boron Carbide Nanocage

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ABSTRACT

Equilibrium geometries, stabilities, and electronic properties of hydrogen (H_2) molecule adsorption at the exterior surface of fullerene-like boron carbide ($B_{16}C_{16}$) were investigated through density functional theory (DFT) calculations. Indeed, sensor applications of such nanocage for H_2 molecule were explored here. H_2 molecule was physically adsorbed at the surface of $B_{16}C_{16}$ nanocage with adsorption energies of -0.13 and -0.15 eV. It was revealed that the electron transport through $B_{16}C_{16}$ was significantly increased in the presence of the H_2 molecule due to the reduced frontier molecular orbitals energy gap. Based on the obtained results, it was expected that $B_{16}C_{16}$ nanocage could work as promising candidates in gas sensor devices of H_2 molecule detections. The results also showed fairly short recovery time and high sensitivity benefits for $B_{16}C_{16}$ nanocage.

KEYWORDS Boron carbide, Fullerene-like, Nanocage, DFT, Gas sensor.

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INTRODUCTION

Since the discovery of C_{60}, several studies have been reported on nanostructures such as nanotubes, nanocages, nanocones, graphene, and etc.[1-5] In addition, many attentions have been focused on boron carbide (BC) nonmaterials such as BC nanotubes, nanocapsules, nanoparticles, and nanocages, which are expected to be useful as electronic devices with high heat-resistance.[6] Fullerene-like BC nanocage has a wide range of attractive properties, such as high temperature stability, low dielectric constant, large thermal conductivity, and oxidation resistance, leading to a number of potential applications as a structural or electronic material.[7] The stabilized geometries of BC nanocages have been studied by many research groups, in which $B_{12}C_{12}$ nanocage has been seen as a favorable structure due to unique configurations of B and C atoms.[8] Owing to the dramatic growth in industrial development and population, the natural atmospheric environment has become more polluted day by day and innovating such gas pollutant removals is almost an essential.[9] Considerable attempts have been dedicated to develop suitable gas sensor materials for continuous monitoring and setting off alarms for chemical vapors present beyond specified levels.[10, 11] Among these gas sensor materials, hydrogen (H_2) is attractive because of its usage in fuel applications.[12-14] The use of H_2 requires an effective, safe, and stable storage medium whereas H_2 storage is still one of the key challenges in developing of such economy.[15] Considerable attentions have been focused on porous

materials such as metal–organic frameworks (MOF's), carbon nanotubes, fullerenes and organic hosts as possible materials for H_2 storage.[16-20] Gas adsorption on nanostructures is a great issue for both essential research and application as gas sensors, fuel storages, and hazardous pollutants removals.[21-23]

Due to such importance, this study was performed to explore interactions between H_2 molecule and a representative model of $B_{16}C_{16}$ nanocage. The main purpose of this study was to achieve fundamental insights into the influence of adsorbed molecule on the structure of nanocage and its related electronic properties, and how these effects could be used to design sensor gas devices. To approach to this purpose, density functional theory (DFT) calculations were performed to investigate the model systems at the lowest molecular and atomic scales by the benefit of such computer-based works for materials characterizations.[24-29]

MATERIALS & METHODS

A representative model of BC nanocage including $B_{16}C_{16}$ consisting of six square, six hexagon and two octagonal rings was investigated for were considered in this work. DFT calculations were performed for achieving optimized geometries employing the M06-2X/6-311G(d,p) computational level without any symmetry constrain using the GAMESS program.[30] Vibration frequencies were also calculated at the same computational level to confirm global minimum for the optimized structures. Analyses such as natural bonding orbital (NBO), density of states (DOS), and frontier molecular orbital (FMO) were done for the optimized models. The value of adsorption energy was defines using eq. (1).

$$E_{ads} = E_{(gas@nanocage)} - E_{(gas)} - E_{(nanocage)} \quad (1)$$

Where $E_{(gas@nanocage)}$ is the total energy of adsorbed H_2 molecule at the surface of nanocage, each of $E_{(gas)}$, and $E_{(nanocage)}$ are for the total energies of singular molecular counterparts. A negative value of E_{ads} could correspond to exothermic adsorption. All results of this work were included in Table 1 and Figs. 1 and 2.

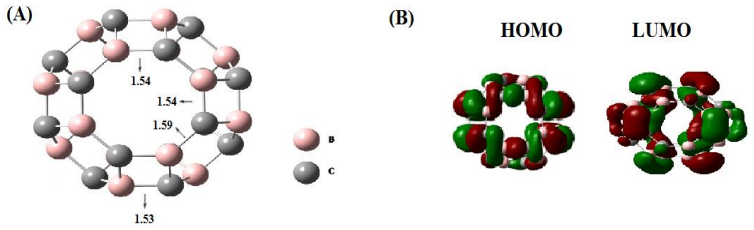

Fig. 1: A) Optimized geometry and B) distribution patterns of HOMO and LUMO for singular $B_{16}C_{16}$ nanocage. Bond distances are in Å.

RESULTS & DISCUSSION

The main purpose of this work was to examine adsorption processes of H_2 molecule, as an explosive gas, at the surface of a representative $B_{16}C_{16}$ nanocage for providing $H_2@B_{16}C_{16}$ cluster formation. To achieve such purpose, DFT calculations were performed in each of optimization step and properties evaluation step to provide required information regarding the purpose problem. It was mentioned that such computer-based works could help to improve insights about the complicated materials systems especially those of nano-related systems. To this aim, the optimized geometries of singular $B_{16}C_{16}$ nanocage was shown in Fig. 1; the B–C bond length was 1.54 for the square ring and it was 1.59 Å for the hexagonal ring. One of important structural features of such nanocage systems are their variety of ring construction making them more proper for various applications. The value of E_g, as the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), was 4.09 eV for the singular $B_{16}C_{16}$ nanocage. As shown in Fig. 1, the HOMO and LUMO of $B_{16}C_{16}$ are localized at the C and B atoms, respectively. We carried out full structural optimization before and after adsorption for each of singular $B_{16}C_{16}$ nanocage and H_2 molecule and $H_2@B_{16}C_{16}$ interacting cluster to provide proper structures for examining the structural and electronic properties and features. To find the most favorable adsorption configurations, H_2 molecule was initially placed at different positions above the nanocage surface with different orientations. Detailed obtained information including values of E_{ads}, NBO charge transfer (Q_T) and ΔE_g (change of E_g of upon the adsorption process) were all listed in Table 1 and they were visually represented in Fig. 2.

As indicated above, several initial configurations were investigated for adsorption of H_2 at the targeted BC nanocage through DFT calculations. The H_2 molecule was initially placed above each of B and C atomic sites, in which the H_2 molecule was oriented perpendicular to the nanocage. Several other configurations of H_2 molecule were placed towards the nanocage surface, in which above the center of tetragonal and hexagonal rings were also tested for the purpose. After full relaxation, the most stable $H_2@B_{16}C_{16}$ complexes were obtained with negative values of E_{ads} of -0.13 and -0.15 eV as shown in DOS plots of Fig. 2.

The content of Table 1 could show that the adsorption processes yielded different features upon adsorption of H_2 at the B atomic site or C one. In this case, structural features such as interacting distance and E_{ads} could help to make sense the capability of such nanocage for H_2 adsorption. Furthermore, electronic feature of Q_T could show the amount of charge transfer between the interacting components revealing possibility of interaction occurrence for the complex system. Additionally, values of E_g and ΔE_g could provide signaling feature for detection of adsorbed H_2 at the $B_{16}C_{16}$ nanocage in the step of $H_2@B_{16}C_{16}$ complex formation. In such process, the signaling change of frontier molecular orbitals variations could help for detecting mode in addition to those changes for providing possibility for occurrence of adsorption process. Besides sensing mode, gas storage is also very much important for the nanocage systems. To approach this aim, proper values of E_{ads} could help to provide such storage systems for gas adsorption processes. For the investigated systems of this work, the results indicated that employing heterogeneous BC nanocage could be even better for such adsorption processes by providing different atomic sites to allow the gas for choosing the favorable atomic site for adsorption. It could be also mentioned that such heterogeneous surfaces might provide somehow ionic system for better interacting modes. As a consequence, the investigated BC nanocage could be proposed for H_2 adsorption regarding sensing and storing modes.

Table 1: The adsorption features.

Configuration	E_{ads} (eV)	Q_T	E_g (eV)	ΔE_g (eV)
A_1	-0.13	0.017	3.59	0.50
A_2	-0.15	0.003	3.60	0.49

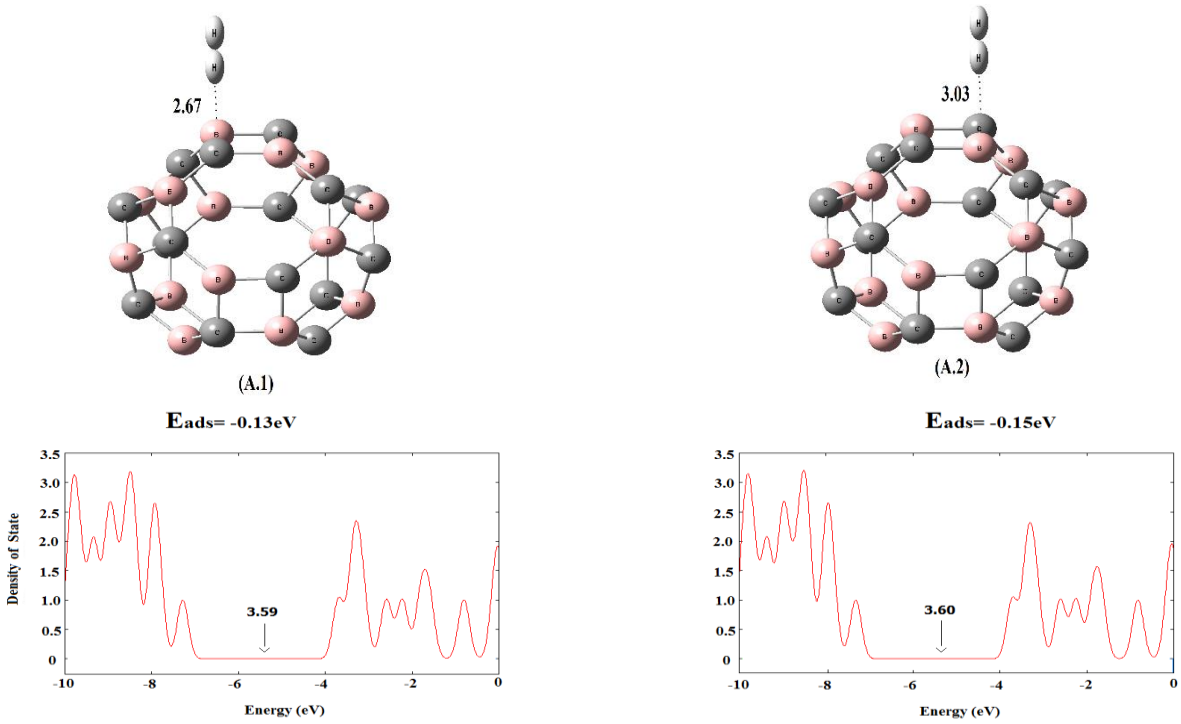

Fig. 2: Optimized structures of stable $H_2@B_{16}C_{16}$ complexes and their DOS plots. Interaction distances are in Å.

CONCLUSION

This work was performed through DFT calculations to study the adsorption of a H_2 gas at the surface of representative $B_{16}C_{16}$ fullerene-like nanocage. Possibility of complex formation of $H_2@B_{16}C_{16}$ cluster were investigated. The values of energy for the most stable configuration of adsorption processes were calculated to be -0.13 and -0.15 eV for H_2 molecule towards B and C atomic sites of heterogeneous surface. In particular, the

fullerene-like BC nanocage was found to be a good candidate for constructing sensor and storage device purposes. Based on analysis of DOS plots, it was found that H_2 molecule adsorption could appreciably increase the electrical conductivity of fullerene-like BC nanocage with reduction of E_g approximately about 15 % than its original value. Hence, the investigated $B_{16}C_{16}$ nanocage could be used as a gas sensor and storage device for H_2 molecule.

DISCLOSURE STATEMENT

The author(s) did not report any potential conflict of interest.

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