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Methane storage capacity of carbon fullerenes and their mechanical and electronic properties: Experimental and theoretical study

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HIGHLIGHTS

- DFT study on methane storage capacity of carbon fullerenes.
- The effect of fullerene diameter was investigated.
- Mechanical properties was investigated using DFT calculation and AFM analysis.
- Three different temperature was selected to examine the trend of Young's modulus.

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ABSTRACT

The storage capacity of carbon fullerenes with confined methane molecules was investigated by means of DFT. Based on our calculations; C_{60} and C_{84} fullerenes with one methane molecule can form a stable complex. The binding energy of C_{60}@$1CH_4$ and C_{84}@$1CH_4$ was negative and equals to-0.638 eV and −0.5593 eV, respectively. C_{180} with twelve confined methane molecules has a stable structure. However, C_{180} tends to store just six methane molecules and the binding energy for the $6CH_4$@C_{180} complex was minimal (−0.256 eV). Regarding obtained results on the electronic properties, the values of the energy gap for $1CH_4$@C_{60}, $1CH_4$@C_{84} and $6CH_4$@C_{180} complexes were 1.1 eV, 0.87 eV and 0.94 eV, respectively. We have also studied the mechanical properties of C_{60}, C_{84}, $1CH_4$@C_{60} and $6CH_4$@C_{180} by the use of DFT and experimental procedure. Moreover, the stability of $1CH_4$@C_{60} and $6CH_4$@C_{180} complexes was studied in the temperature range between 300 K and 1200 K. We found that the complex structures were slightly distorted and the values of Young's modulus of them with increasing in the temperature value decreased significantly.

1. Introduction

Developing in human society and high growth of different industries has led the fossil fuels such as coal, petroleum, etc. to be consumed with a pretty fast speed. Therefore, nowadays utilizing new and useful alternative sources of energy seems to be an urgent issue. Accordingly, hydrogen and natural gas (which is mostly methane), are generally considered to be convenient and less polluting alternatives [1–3]. Carbon dioxide is currently the most significant contributor to greenhouse gases, and more than 60% of current global warming effects are due to it. In addition to carbon dioxide, methane is also an important greenhouse gas, so using of methane as an alternative fuel can decrease the effects of this gas. This issue is of great significance for protecting the environment [4]. Methane constitutes two-thirds of fossil fuels, but it has remained the least-utilized fuel [3]. Methane is a preferable fuel because it burns more cleanly comparing to other fossil fuels and has the largest hydrogen to carbon ratio. In addition to its natural abundance, it is comparatively safer than most of the other fuels [5], and it has lower carbon emissions than petroleum [6]. However, a significant drawback of methane is that the volumetric energy density of compressed methane only one-third of that of gasoline. For this reason, it is necessary to find new materials to enhance the volumetric density of stored methane which leads to expand the role of natural gas as a transportation fuel. Hence, the effective encapsulation of natural gas has become a primary goal [7]. Porous materials provide an alternative which make storing possible at ambient temperature and reasonable pressure [8]. Carbon

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nanostructures such as fullerenes, single-walled nanotubes (SWNT), and multi-walled nanotubes (MWNT) [9] have been used to expand alternatives for clean and supportable energy technologies [10]. Among the beneficial properties of carbon nanostructures, the feasibility of synthesizing endohedral fullerenes or nanotubes with various atoms and molecules is useful for various applications [11]. Moreover, carbon fullerenes are one of the most stable and well-known nanoscale molecular structures. Carbon fullerenes consist of a sheet of connected hexagonal rings separated by pentagonal and/or heptagonal rings that are useful for creating spherical cage-like structures [12]. Among various fullerenes, C_{60} is the most widely used, because of its technological availability and stability when modified. Therefore, it has been selected as a model by scientists for a wide range of researches, such as studying its physical and chemical attributes and operating characteristics of compounds in this class [10]. Many studies have also investigated the structural capability of fullerenes and their electronic properties in storage applications [13]. One remarkable aspect of fullerene cages is that, their cavities are large enough [14] to trap atoms or small molecules, so they can be used in different applications, for example the storage of certain gases and even molecular electronics [10]. However, it was soon found that the confinement of a guest in the cavity of a fullerene cage would affect both the host and the guest [15]. Notably, fullerenes, have a finite capacity to retain a certain number of endohedral substituents due to their size [10].

In recent years, many researchers have been published regarding the storage of methane and hydrogen molecules in different porous structures in order to be used as alternative fuels [11,13,16–28]. Ganji et al. have studied the formation of an endohedral complex between methane and Si_{60} and C_{60} [20]. They determined that C_{60} is only able to store one methane molecule in its cavity, while Si_{60} can store up to eight methane molecules in its inner cavity and also has a stable structure. In another work, Ganji and et al. [29], have studied the hydrogen storage capacity of C_{60} and $C_{48}N_{12}$, and showed that, these structures are capable of incorporating two hydrogen molecules inside the cavities of their nanocages. Pupysheva et al. [11] have investigated the encapsulation of hydrogen molecules inside $C_{60,}$ and concluded that, C_{60} with a maximum of 58 hydrogen atoms has a metastable structure. Konstas et al. [16] have investigated the methane storage in metal organic frameworks (MOFs). They concluded that MOFs have remarkable potential for the high density storage of natural gas. In another research about MOFs, Thornton et al. [17] have studied methane and hydrogen storage materials involving the incorporation of magnesium-decorated fullerenes within MOFs. Their model and the new approach that they used in their research have great results; including the highest reported value of volumetric methane uptake for any materials. Moradi et al. [46] have investigated the effect of sodium on the methane storage of BC_3 nanosheet. They have shown that decorated of Na atom on surface of sheet increased the methane storage capacity of this system [46].

Furthermore, many experimental and theoretical researches have been performed on physical and mechanical properties of fullerene and other nanostructures. Kizuka at el. have studied the Young's modulus of crystalline nanotubes composed of C_{60} molecules with high-resolution transmission electron microscope. They have found that the Young's modulus of the nanotube was around 62–107 GPa [30]. In another research, QIU et al. have investigated the physical and mechanical properties of C_{60} fullerene sample under high pressure and high temperature condition with a designer Diamond Anvil Cell. The measured value of Young's modulus in their experiment was estimated to be about 1215 ± 50 GPa by the use of nanoindentation technique [31]. In theoretical study, Zhou et al. have investigated the mechanical properties of single-walled carbon nanotube (SWCNT) using first-principles cluster method via the framework of local density approximation. Young's modulus of this system was determined to be 0.746 TPa [32].

In this work, we focused on the methane storage capacity and stability of three carbon fullerenes: C_{60}, C_{84} and C_{180}. After full structural optimization, we investigated the capability of each fullerene with confined methane molecules and also stability of formed complexes. For more investigation on the changes in the stability of empty cages and their complexes, we studied electronic properties of the carbon fullerenes before and after methane encapsulation based on first-principle density functional theory (DFT) calculations. Moreover, we evaluated the Young's modulus of C_{60} fullerene both experimentally and theoretically which will be discussed in following with full details. The stability of these complexes has been determined at different temperatures with molecular dynamics simulation to provide more details about most stable structures with confined methane molecules.

2. Experimental section

2.1. Materials

Crystalline fullerene-C_{60} utilized in this study with higher than 99.5% purity was provided from Sigma Aldrich, Saint Louis, USA. Si wafer (p-doped, polished <100 > surface, 4 in, one side polished, 500 μ thickness) as a substrate for thermal evaporation process (PVD) and physical method of thin film deposition (TFD) was used.

2.2. Samples preparation

Silicon wafers were cut into 1 cm × 1 cm pieces and were cleaned by heating up to about 1000 K under vacuum. Then C_{60} powder was put in the Tungsten crucible and placed in the embedded location into a chamber vacuum that provided a vacuum of 10^{-6} torr. The rate of deposition was adjusted to 3 Å/sec. At the end of PVD process a Homogenous brown layer with 100 nm thickness was created on the slices of Si wafer. For measuring Young's modulus, we used these deposited layers with Force-Spectroscopy analysis by the Atomic Force Microscopy (AFM).

2.3. Characterization

Force-Spectroscopy analysis of the samples was performed by Si tip with radius about 8 nm, the cantilever series was HQ: CSC17 and was on the contact mode. To obtain Young's modulus, the cantilever tip was brought into contact with the fullerene sample that deposited on the wafer by PVD method inside the microscope and then the cantilever tip was pulled back to release the force. This procedure was repeated at room temperature several times with the same sample. The applied force to the sample was measured and results were used in AFM captured as a Force-deformation curve. The spring constant of the cantilever was measured to be 0.18 N/m.

3. Computational details

Our computational study consists of two parts: density functional theory and molecular dynamics simulation. We investigated the properties of carbon fullerenes containing 'n' methane molecules with DFT. Some of our calculations were performed with OpenMX [33–35], SIESTA [36] and DFTB+ [37] code, and the results were compared to the values collected from ORCA code based on the framework of the B3LYP-TZVP scheme [38]. In the geometric relaxation procedure using ORCA code, entirely atoms in the structures were fully optimized, followed by verifications using