

Simulation of hydrogen adsorption on carbon nanotubes with different chirality parameters

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Abstract. The hydrogen adsorption properties and surface charge distribution of single-walled carbon nanotubes (SWCNTs) with chirality parameters of (5,5), (9,5), (9,9) were investigated using molecular dynamics methods. Relation between maximum hydrogen uptake and SWCNT structural properties was investigated. It was shown that surface charge distribution of chiral nanotubes could not be compensated for the same amount of steps that leads to fully neutral CNT with armchair structure.

1. Introduction

Rare-earth elements are actively used for formation of nanotubes at electrochemical synthesis from carbon fragments of graphene type in the environment of ions of rare-earth metal [1]. This way of production has considerable impact on structure of carbon nanotubes and is reflected in functional properties. It demands attentive studying, including methods of mathematical modeling.

The present level of computer science and software development provides for significantly wider application of computational simulation as compared to studies conducted just a decade ago. Until recently, one of the most popular basic simulation methods for various structures and compounds was the calculation of the system molecular dynamics under various external conditions. These conditions, in their turn, were simulated by limiting the computational region and variations of the system initial state through setting the force-field, simulated atoms and molecules.

A large number of software solutions and algorithms for the implementation of various simulation conditions were developed. For instance, the Monte Carlo method was proposed as a technique to improve the efficiency of calculations. This method allowed one to reduce significantly the calculation time without a considerable loss in the accuracy of the end result [2-4]. However, all molecular dynamics methods used to describe the force-field and interatomic interactions do not account to the full extent for the electronic structure of individual atoms. Therefore, in some cases, it is impossible to describe all the processes occurring in the system. For example, without considering the electronic properties of atoms it is rather difficult to describe accurately various chemical reactions and magnetic properties of various compounds. Furthermore, when considering nanostructured systems, various quantum effects can be very important, and their electronic structures may significantly differ from the electronic structures of solid bodies. There is also a limitation with regard to a range parameter in interaction. The wider range makes it difficult to select the conditions and parameters of calculation, and also reduces the universality of potential.



Therefore, comparatively recently it has been proposed to use quantum-mechanical calculations for multinuclear and many-electron systems to describe more accurately the processes occurring in the system [5].

The analysis of the adsorption characteristics of various carbon adsorbents including those based on carbon nanotubes (CNT) raises the issue of how to account for their electronic properties, for example, in the case that a CNT structure contains other functional groups ($-\text{NH}_2$, $-\text{OH}$, etc.) in addition to carbon atoms, or when considering more complex interactions. Similar problems are currently solved using quantum chemistry methods such as the variations of the density functional theory (DFT) and the computations according to the Hartree–Fock method. At the moment, some results of such calculations for a limited number of structures based on CNT are available. For instance, in [6], it was shown that the use of CNT functionalized with OH and NH_2 groups can significantly improve the adsorption properties of these materials. There are also published data on the calculation of the adsorption properties of CNT using the quantum-mechanical methods that demonstrate how some parameters of the electronic and molecular structures can affect their end properties [7-8].

However, the present data on complex studies of the adsorption properties and electronic structure of CNTs with different chirality obtained using quantum-mechanical calculations and molecular dynamics method are insufficient to compare the calculated results with experimental data [9-12].

The approach proposed in this paper will help to provide a more complete picture of adsorption properties for the basic types of CNT structures.

2. Calculation Method

This paper presents molecular dynamics simulation for hydrogen adsorption process on the CNT structures calculated using LAMMPS [13] software with AIREBO [14] potential for carbon-hydrogen bond simulation. Surface charge distribution was obtained with Avogadro [15] molecular editor.

The adsorption characteristics and structural properties were simulated for three basic types of single-walled nanotubes 2 nm in length and the following chirality parameters: $n = m = 5$ (armchair type), $n = 9, m = 5$ (chiral type) and $n = 9, m = 9$ (armchair type). Figure 1 shows the structures.

The adsorption characteristics were simulated for three types of structures: a single nanotube (a), "square" configuration (b) and "triangle" configuration (c). Figs. 2 and 3 give the types of configuration.

The calculation was performed for a simulation cell of SWCNTs square array and SWCNTs triangle array as well as is shown in Figures 2-3. The modeling was performed for a temperature of 77 K, and the initial pressure of hydrogen varied from 0.1 to 50 MPa. The simulation step was 0.5 fs. The periodic boundary conditions were used in all three directions. The temperature of 77 K corresponds to the boiling point of liquid nitrogen. Therefore, it was used to compare the obtained results with the experimental data, which are often obtained at this temperature. An NPT assembly was used for calculation, because it was necessary to control the pressure in the system. Fifty randomly distributed hydrogen molecules were introduced into the cell so that the minimum distance between the molecules was not less than 0.5 nm. Then the structure was subjected to optimization for 5000 steps in order to determine the nearest energy minimum of the system, after which $1 \cdot 10^6$ steps of molecular dynamics were calculated.

Based on the simulated results, the adsorption isotherms were calculated within the pressure range of 0 to 5 MPa by the molecular dynamics methods and the corresponding energy minima were calculated by the quantum methods.

3. Results and discussions

Based on the calculated data, the adsorption isotherms were constructed for each type of the nanotubes (Figures 4-6).

The highest adsorption values are typical for the nanotubes with larger diameters, i.e. the structures with the parameters of (9,9) and (5,5). Moreover, the "chiral" nanotubes with the structure parameters

of (9,5) not only have larger diameter, but are characterized by a large number of uncompensated bonds located at both ends of the structure. This means that adsorption is much more probable due to an increased energy of carbon atoms having the smallest number of neighbors.

Isotherms for “square” and “triangle” pattern differ from single SWCNT mostly in highest hydrogen uptake values. The “triangle” configuration shows the lowest hydrogen uptake due to the smallest distance between neighbor CNTs.

Here, we consider the distributions of surface charge of carbon nanotubes before and after adsorption simulation.

Figure 7a shows the model of the (9,5) CNT structure before the adsorption with the generated map of surface charge. The uncompensated negative charge is shown red and the uncompensated positive charge is shown blue. The neutral atoms are shown gray. As it is seen from the Figure 7a, the structure is characterized by a large number of uncompensated negative charges. Therefore, favorable conditions for the adsorption of positively charged particles, including atomic hydrogen, are created.

Figure 7b demonstrates that, after the hydrogen adsorption, the compensation of negative charge is observed at the edges of the nanotube. This results in an overall reduction of the surface energy of the structure. Similar changes in the surface charge distribution are observed for other types of the simulated structures; however, the example of chiral nanotubes with the parameters of (9,5) most clearly demonstrates the partial compensation of the surface charge as a result of adsorption.

Figures 8a and 8b show the models of the surface charge distribution for the nanotubes with the parameters of (5,5) before and after the adsorption of hydrogen, respectively. It is seen that, in this case, after the adsorption, an excess negative charge of the structure is completely compensated. This is also an evidence for the formation of stable carbon-hydrogen chemical bonds, which is the expected result due to the presence of uncompensated surface bonds in the nanotubes.

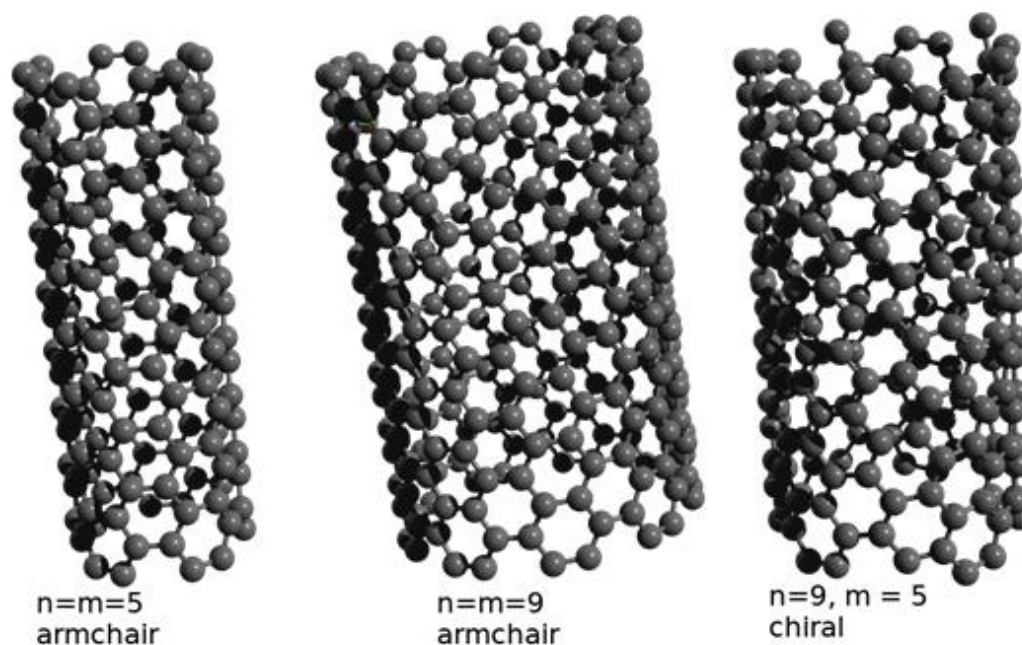


Figure 1. Models of nanotube structures (5,5), (9,9), (9,5)

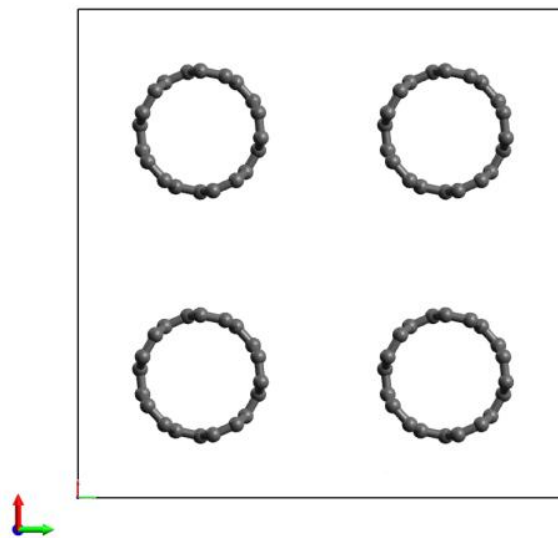


Figure 2. "Square" Configuration of Nanotubes

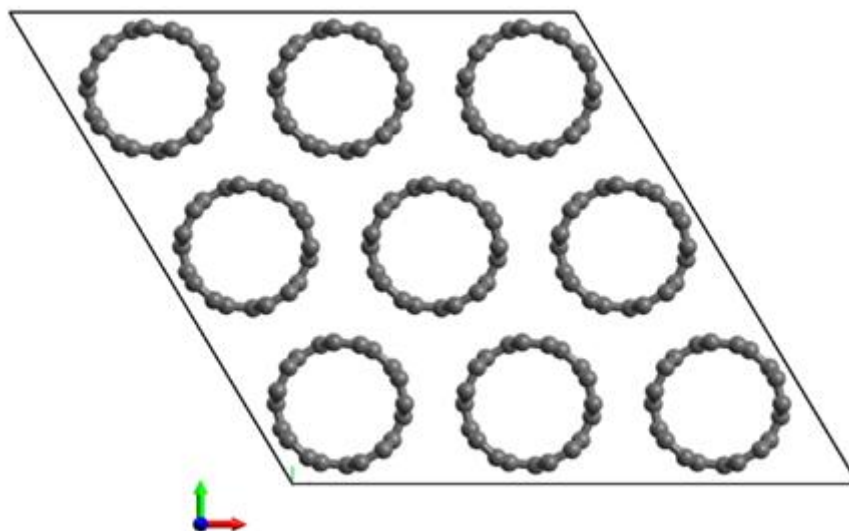


Figure 3. "Triangle" Configuration of Nanotubes

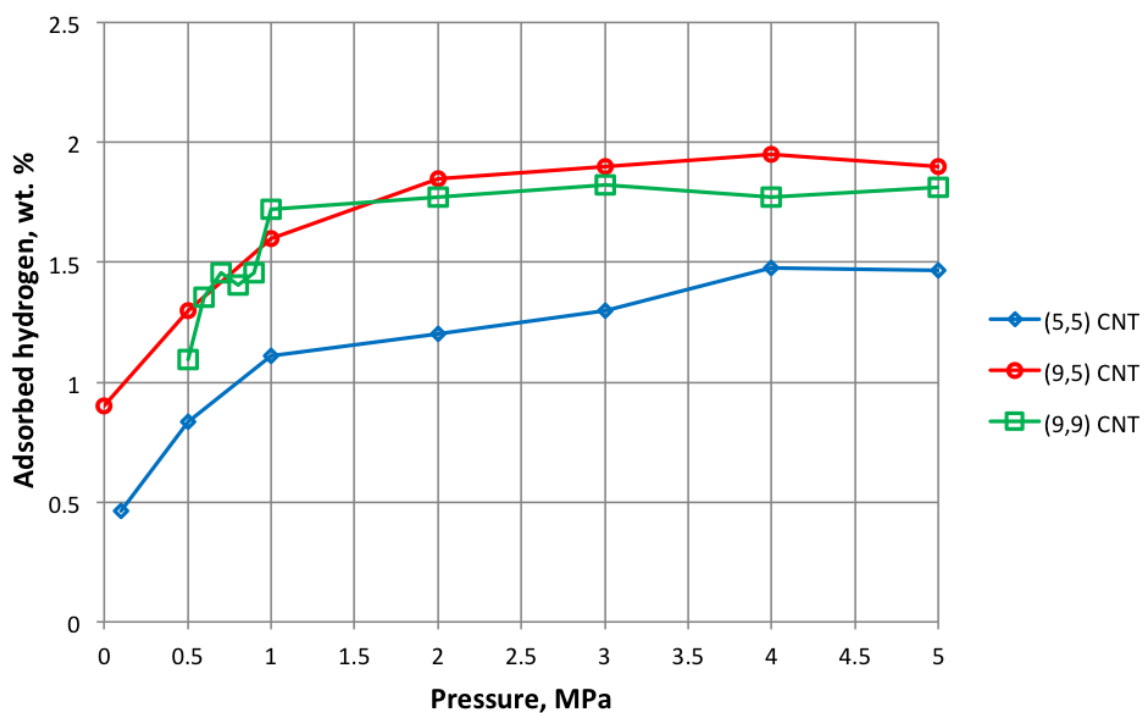


Figure 4. Adsorption isotherms for a single nanotube with the parameters of (5,5), (9,5), (9,9)

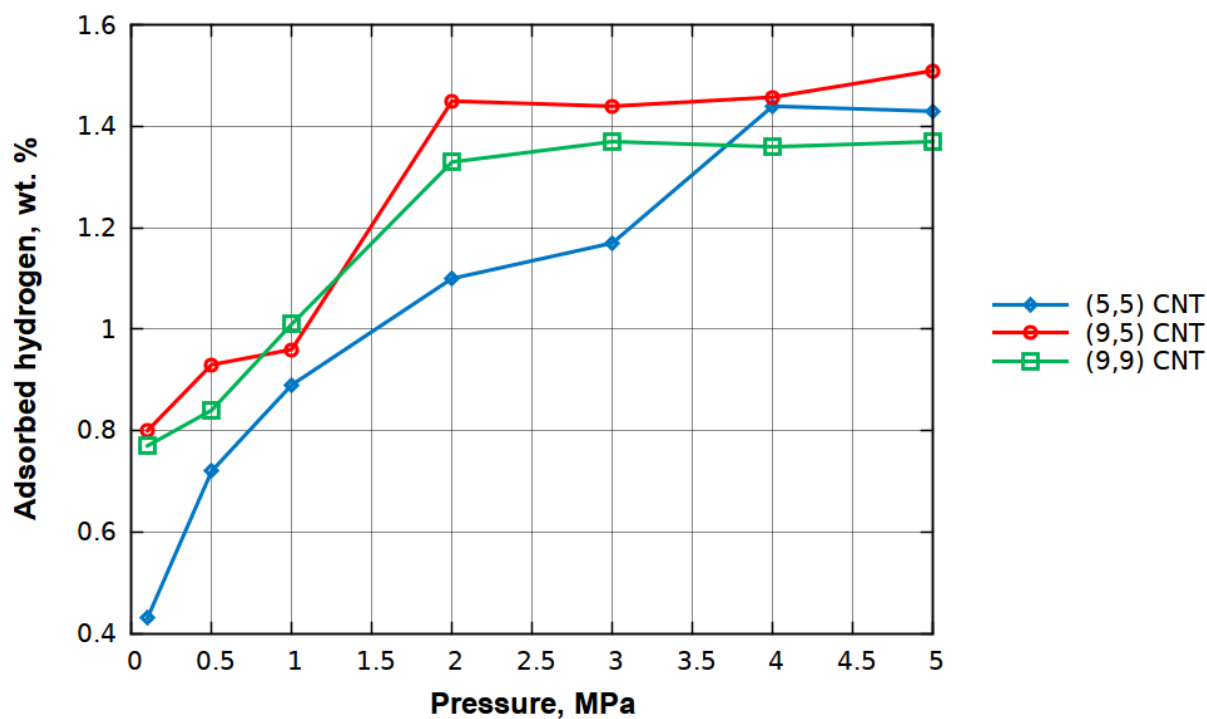


Figure 5. Adsorption isotherms for a triangle array of SWCNT (5,5), (9,5), (9,9)

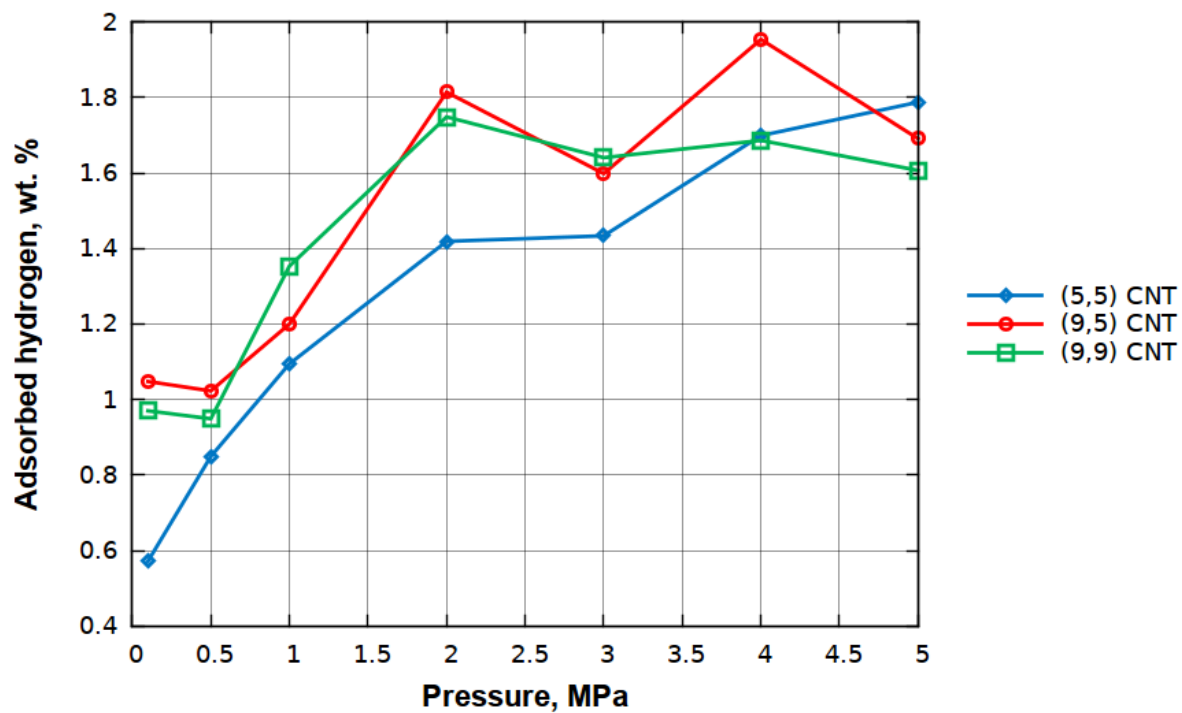


Figure 6. Adsorption isotherms for a square array of SWCNT (5,5), (9,5), (9,9)

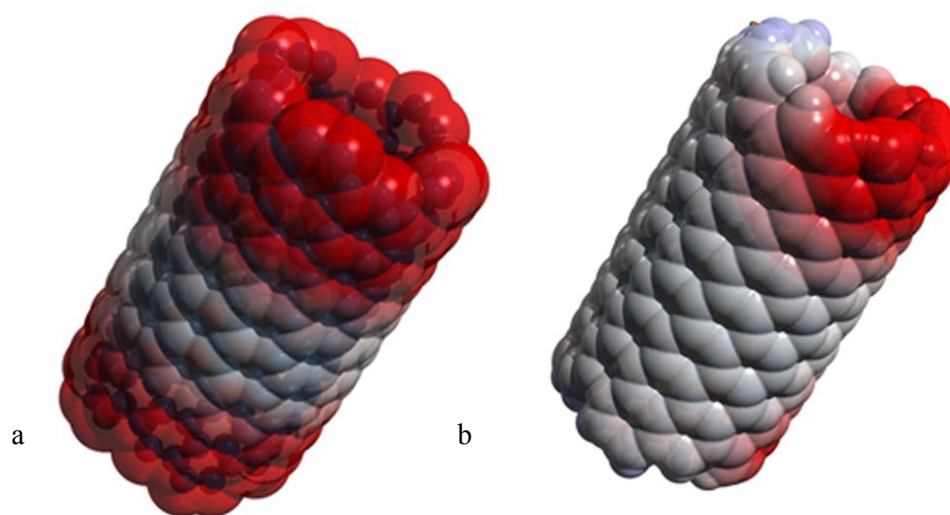


Figure 7. Model of surface charge (electrostatic potential) distribution for a carbon nanotube with the parameters of (9,5) a) before hydrogen adsorption and b) after the hydrogen adsorption

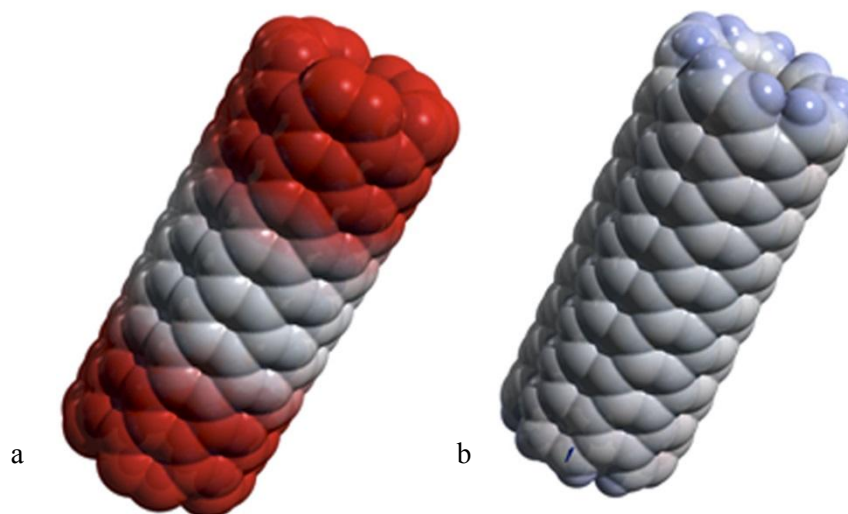


Figure 8. Model of surface charge distribution for a nanotube with parameters (5, 5) a) before hydrogen adsorption and b) after the hydrogen adsorption

4. Conclusions

Based on these results, we can conclude that the structures under consideration demonstrate rather similar properties in the context of the applied calculation methods. An increase in the adsorption with increasing diameter and number of defect of nanotubes (increasing number of uncompensated surface bonds) is also clearly seen. At the same time, when considering the simulated structures, it is seen that the hydrogen molecules are first located at the free ends of the nanotubes and then adsorption can be observed in the middle of the nanotube structure at sufficiently high pressure in the system. The inner surface of the nanotubes is practically unfilled.

As a result of the adsorption interaction of the simulated structures with hydrogen, the partial compensation of surface charge is observed in the case of chiral nanotube and full compensation in the case of nanotube of the armchair type.

5 Acknowledgements

This research was supported by the Russian Federal Target Program "Research and Development in Science and Technology Priority Development Fields for 2014–2020" (grant agreement No. 14.575.21.0087 dated 21.10.2014, Project ID - RFMEFI57514X0087).

References

- [1] Yao M, Liu B, Zou Y, Wang L, Cui T, Zou G, Li J, Sundqvist B 2006 Effect of rare-earth component of the RE/Ni catalyst on the formation and nanostructure of single-walled carbon nanotubes *J Phys Chem B* **110** **31** 15284-90
- [2] Mahdizadeh S J 2014 Hydrogen storage on silicon, carbon, and silicon carbide nanotubes: A combined quantum mechanics and grand canonical Monte Carlo simulation study *Int. J. Hydrogen Energy* **39** 1719-31
- [3] Cheng H, Cooper A C, Pez G P, Kostov M K, Piotrowski P and Stuart S J 2005 Molecular dynamics simulations on the effects of diameter and chirality on hydrogen adsorption in single walled carbon nanotubes *J. Phys. Chem.* **109** 3780-86
- [4] Ahadi Z, Shadman M, Yeganegi S and Asgari F 2012 Hydrogen adsorption capacities of multiwalled boron nitride nanotubes and nanotube arrays: a grand canonical Monte Carlo study *J. Molecular Model* **18** 2981-91
- [5] Khan M Z and Khan M Z 2012 Computational study of hydrogen adsorption on potassium-decorated boron nitride nanotubes *In. Nano Letters* **2** 2-7

- [6] Soleymanabadi H and Kakemam J 2013 A DFT study of H₂ adsorption on functionalized carbon nanotubes *Physica E: Low-Dimensional Systems and Nanostr* **54** 115-117
- [7] Ghasemi A S 2012 Highly Sensitive Single-Walled Carbon Nanotube (5, 0) for Adsorptions Gases CO₂, CO and N₂: A DFT Study *International Journal of Chemtech research CODEN* **4** 1302-08
- [8] Ashrafi F 2010 Optimization of carbon nanotubes for nitrogen gas adsorption *J. Appl. Sci. Eng. Tech* **2(6)** 547-551
- [9] Al-Ghamdi A A, Shalaan E, Al-Hazmi F S; Faidah A S, AlHeniti S; Husain M 2012 Adsorption Sites of Hydrogen Atom on Pure and Mg-Doped Multi-Walled Carbon Nanotubes *Journal of Nanomaterials* **2012** 1-5
- [10] Barghi S H 2014 Chemisorption, Physisorption and Hysteresis during Hydrogen Storage in Carbon Nanotubes *Int. J. Hydrogen Energy* **39(3)** 1390-97
- [11] Zhou L G and Shi S Q 2002 Molecular dynamic simulations on tensile mechanical properties of single-walled carbon nanotubes with and without hydrogen storage *Computational Materials Science* **23** 166-174
- [12] Hong Z, Shaoqing W and Huiming C 2004 Effect of chemical potential on the computer simulation of hydrogen storage in single walled carbon nanotubes *Sci. in China Ser. B Chemistry* **47(3)** 222-227
- [13] Plimpton S 1995 Fast Parallel Algorithms for Short-Range Molecular Dynamics *J. Comp. Phys* **117** 1-19
- [14] Stuart S J, Tutein A B and Harisson J A 2000 A reactive potential for hydrocarbons with intermolecular interactions *J. Chem. Phys.* **112** 6472-86
- [15] Hanwell M D, Curtis D E, Lonie D C, Vandermeersch T, Zurek E and Hutchison G R 2012 Avogadro: An advanced semantic chemical editor, visualization, and analysis platform *Journal Cheminformatics* **4** 1-17