



Research Paper

Simulation study on atomic hydrogen adsorption in multi-layer graphenes

Accepted 21th February, 2019

ABSTRACT

Graphenes is a new type of nano material with unique structure and excellent properties, showing great potential as a hydrogen storage material. In this paper, the structure and hydrogen storage properties of graphenes were studied using material-studio 7.0. Two six-layer graphene structure models were built based on two different modeling methods provided by the software. Simulative calculation of hydrogen storage performance of the two models was conducted under the condition of constant temperature (77 K) and increasing pressure (10 Kpa to 100 Mpa). Calculation results showed that hydrogen appeared to be gathered in layers parallel to graphenes with proper distances when attached to graphene. At 77 K, 20 Mpa pressure enabled the most effective hydrogen adsorption. Under this condition, the volumetric density of hydrogen storage in multi-layer graphenes reached 95 kg/m³ and the mass fraction of hydrogen storage was up to 19 wt%. Hydrogen storage capabilities of two graphene models were almost the same.

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Key words: Graphene, hydrogen adsorption, simulation.

INTRODUCTION

Graphene, a single layer of carbon atoms in a honeycomb lattice, offers several fundamentally superior properties that make it a promising material for a wide range of applications, particularly in electronic devices. Its unique form factor and exceptional physical properties potentially enable an entirely new generation of technologies beyond the limits of conventional materials.

It is generally known that the amount of hydrogen adsorption is proportional to the surface area of graphene. Graphene has become the most promising candidate for hydrogen storage because it is lightweight chemically stable and has high specific surface area. Dimitrakakis et al. (2008) from Greek University designed a new 3D carbon material with adjustable pore sizes, which was called pillared graphene. When this new carbon material was mixed with lithium atoms, its hydrogen storage capacity was as high as 6.1 wt%. Ataca et al. (2009) mixed graphene with calcium atoms and obtained a hydrogen storage capacity of 8.4% (wt) using the first principle method and *ab initio* calculation. In addition, the authors found out that molecular hydrogen bond allow hydrogen absorption and desorption in room temperature, while Ca stays on the

graphene surface for recycling. These results have promoted the research on graphene hydrogen storage one step forward.

Previous studies have shown that physical properties of different graphene systems calculated by density functional theory (DFT) are consistent with experimental results (Kim et al., 2005; Sahaym and Norton, 2008; Cabria et al., 2005; Rojas and Leiva, 2007; Ataca et al., 2008; Dag et al., 2005; Liu et al., 2010; Park and Chung, 2010; Ouyang et al., 2011; Xiao et al., 2012; Shunfu, 2016), but most of the graphenes are either single-layer or bi-layer systems. As such in this paper, the structure and hydrogen storage capacities of multi-layer graphenes were studied using Material-studio 7.0 software.

MODELING

There are two ways to construct graphene models in Material-studio 7.0, but the unit cells in these two construction methods are different. Although the volume of cells was the same, the number of nodes varies and the

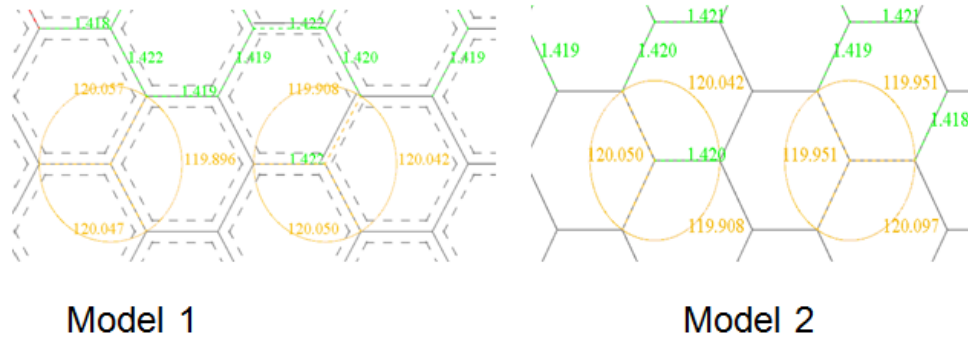


Figure 1: Cellular structures and bond parameters for the two models.

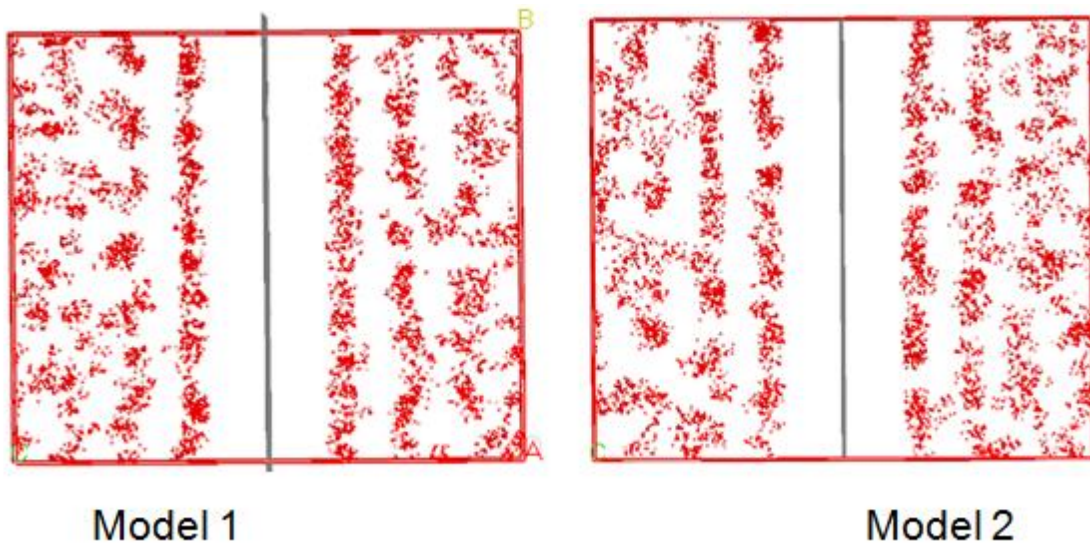


Figure 2: Profile of graphene after hydrogen adsorption.

bond type is different. In this paper, the structure and hydrogen storage properties of these two models were calculated and compared in the same condition.

To construct the first model, the double-layer model of graphene with layer spacing of 0.34 nm was obtained by importing a built-in model in the software (file - Import - structure - ceramics - graphite.msi). Thereafter, the model was expanded into 6 layers, in which one layer was selected and moved to the center of the model. The thickness of the model was 0.68*3 nm. For the second model, the first step was to build the unit cell by choosing the 183rd cell type. The parameters of the cells were set to 2.46, 2.46 and 3.4. The carbon atoms were then added to the cell and the coordinates set to 0.333, 0.667 and 0.500. It was expanded in 6 layers to obtain the cell with thickness of 0.34 nm. Hence, its thickness was the same as that of the first model.

The next step was to determine the number of nodes in two models. To have similar volumes, the number of nodes in two models was expanded to 145 and 128, respectively. To stabilize the models, their geometric structures were preliminarily optimized. Before optimization, the bond

angle was 120 DEG and the bond length was 0.142 nm (Figure 1). Obviously, the first model displayed large number of nodes on the edge, while the second model had none. After the optimization of the geometric structures, both bond lengths and bond angles showed slight changes (Figure 1).

CALCULATION AND ANALYSIS

The simulation calculation of the hydrogen storage capacities of these two models was performed under the condition of constant temperature 77 K and increasing pressure from 10 Kpa to 100 MPa.

The profile of graphene after hydrogen adsorption was shown in Figure 2, in which the red dots illustrated the position where hydrogen might be distributed. A clear observation was that the distribution of hydrogen in these two models was nearly identical; when hydrogen was attached to graphene, it was distributed in layers parallel to the graphene with certain distances. Figure 3 shows the

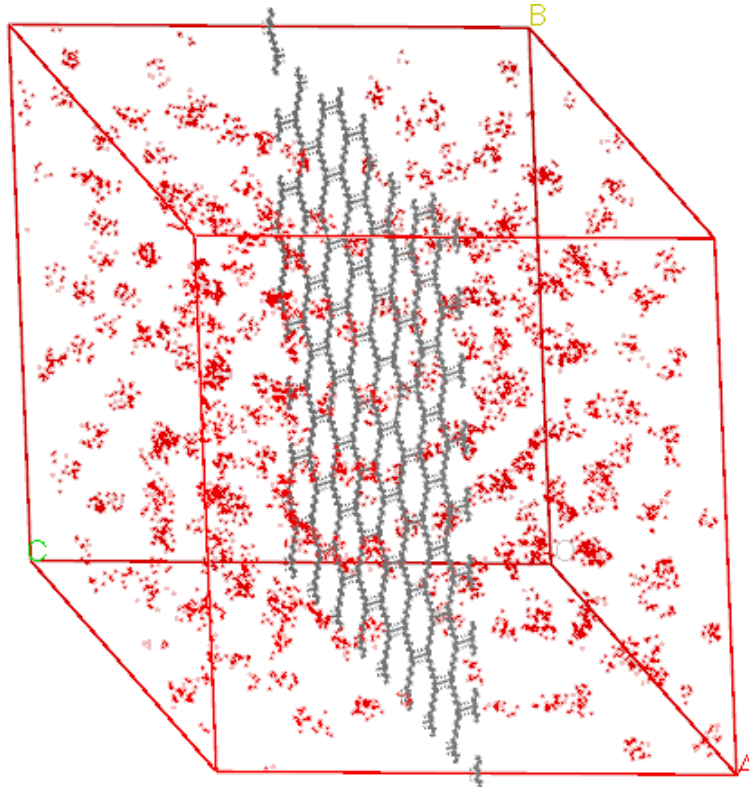


Figure 3: The three-dimensional hydrogen distribution map of grapheme.

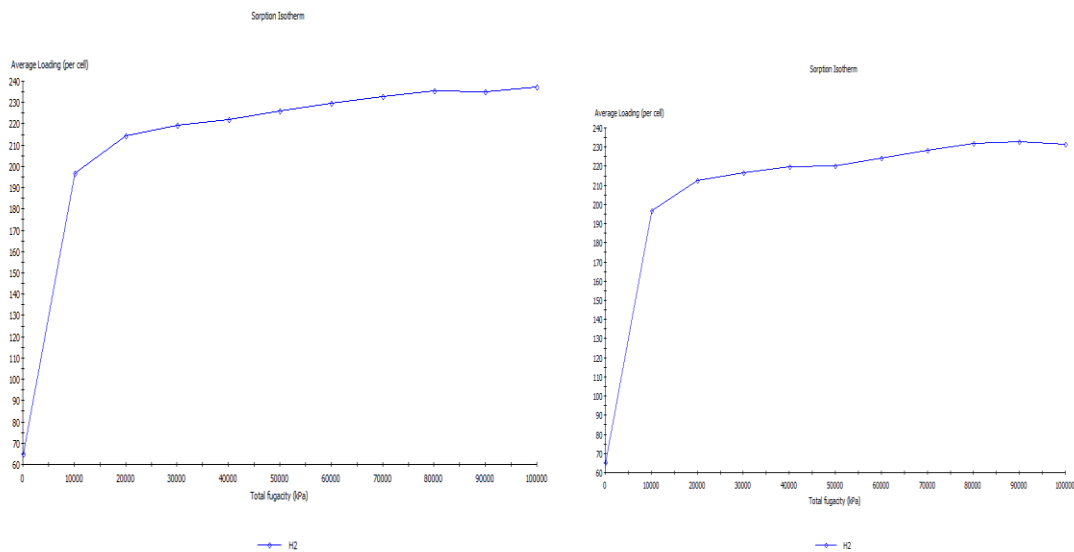


Figure 4: The change of hydrogen adsorption capacity with pressure for two graphene models.

three-dimensional hydrogen distribution map of graphene.

At temperature of 77 K, the change of hydrogen adsorption capacity of two graphene models against pressure (10 Kpa to 100 MPa) was illustrated in **Figure 4**. When the pressure was under 10 MPa, the hydrogen adsorption capacity rapidly increased with pressure.

Within the range of 10 to 20 MPa, the hydrogen storage capacity of graphene showed a slow increase. When the pressure rose to above 20 MPa, the increase of hydrogen adsorption capacity was rather limited. This indicates that the pressure of 20 Mpa allows the most effective hydrogen adsorption. Under the same pressure, no distinct difference

Table 1: Comparison between model 1 and 2 at 77 K, 10 and 100 MPa.

Variable	Average number of hydrogen storage		Relative molecular mass of hydrogen		Molar mass of hydrogen (kg)		Mass fraction (wt%)		Volume of the model (m ³)		Volumetric density of hydrogen storage (kg/m ³)	
	10 MPa	100 MPa	10 MPa	100 MPa	10 MPa	100 MPa	10 MPa	100 MPa	10 MPa	100 MPa	10 MPa	100 MPa
Model 1	196.9125	237.492	3393.825	474.984	65.40×10 ⁻²⁶	78.875×10 ⁻²⁶	18.46	21.44	6.84296×10 ⁻²⁷	6.84296×10 ⁻²⁷	95.57	115.264
Model 2	196.7764	233.002	393.55286	466.004	65.35×10 ⁻²⁶	77.384×10 ⁻²⁶	20.40	23.28	6.84453×10 ⁻²⁷	6.84453×10 ⁻²⁷	95.48	113.06

in hydrogen adsorption capacity was observed between two graphene models.

Table 1 shows that under the condition of 10 and 100 MPa, the quality fraction and the volumetric density of hydrogen storage were calculated and compared between the two models.

As can be seen from the calculations, under the condition of 77 K and 10 MPa, the hydrogen storage capacity of the two models was nearly the same, with the volumetric density of hydrogen storage in single layer graphene reaching 95 kg/m³. When the temperature remained constant and the pressure was increased to 100 Mpa, the volumetric density of hydrogen storage was higher than 113 kg/m³, and the hydrogen storage capacities of the two models were almost the same. The changes of mass fraction of hydrogen storage followed a similar trend. Our result is higher than that reported by Pan et al. (2013) (9.51 wt%).

CONCLUSIONS

Two models of six-layer graphenes were built in this study. Large number of nodes was found on the edge of the first graphene model, while none was found in the second model. However, these two models shared the same structural parameters, like the bond length and bond angle of the unit cell. The results of the simulative calculation in this study revealed that hydrogen was distributed in layers

parallel to graphene with certain distances when attached to graphene. At 77 K, 20 Mpa pressure allowed the most effective hydrogen adsorption. Under this condition, the volumetric density of hydrogen storage in multi-layer graphenes could reach 95 kg/m³ and the mass fraction of hydrogen storage was up to 19 wt%. Two different models of graphene shared nearly the same hydrogen storage capacity.

ACKNOWLEDGEMENT

The financial support of the project by Shenzhen Science and Technology Plan (No. JCYJ20170817112916883) is acknowledged.

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