



Effect of external pressure on the hydrogen storage capacity of a graphene flake: molecular dynamics

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The hydrogenation process of a crumpled graphene flake under the temperature and pressure is calculated by molecular dynamics. A graphene flake is placed in a hydrogen atmosphere containing both atomic and molecular hydrogen and exposed at finite temperature and pressure in an isothermal-isobaric (NPT) ensemble. Results show that the best gravimetric density is achieved at 77 K and external pressure of 140 atm. However, the increase in the gravimetric density at 77 K is due to the physical adsorption of hydrogen molecules, i.e., van der Waals forces are formed between the carbon surface and H₂ molecules. At room temperature, the number of H atoms that formed a covalent bond with the edge C atoms increases during exposure at this temperature. The molecular dynamics simulation demonstrates that different types of hydrogen adsorption by a graphene flake predominate at two temperatures: at 77 K, physical adsorption plays the main role, and at 300 K, chemical adsorption. And the combination of high external pressure and low temperature makes it possible to achieve high values of a hydrogen sorption.

Keywords: molecular dynamics, graphene flake, hydrogenation, hydrogen energy.

1. Introduction

In recent years, hydrogen energy has been considered as an important area of research because hydrogen is a more environmentally friendly material compared to other energy carriers. The use of hydrogen as an energy source leads to zero environmental pollution since only heat and water are the by-products during the process of energy release, which are, if necessary, can be reused [1]. However, there are a range of problems associated with the storage and transportation conditions. Since hydrogen in the gaseous state has a rather low density (0.0898 kg/m³ under normal conditions) [2–4], it is necessary to be increased by: (I) cooling; (II) increasing of the pressure; or (III) reducing the repulsive interaction between hydrogen molecules due to its interaction with atoms of other substances. Low temperatures (20 K) or high pressures (700 atm.) are difficult to implement in the industrial use [5]. Besides, it is unsafe and inefficient from an economic point of view. Therefore, the greatest interest of the modern scientific community has been associated with the search of new materials for the storage and transportation of hydrogen under normal conditions. The US Department of Energy and the International Energy Agency had decided that such material should enjoy a hydrogen sorption capacity of at least 5–6 wt.% in the temperature range of 233–333 K and at normal pressure [6, 7].

As a medium for hydrogen storage and transportation, crumpled graphene (CG) is a promising material, since it has a large specific surface area and high gas adsorption

rate [8–10]. Such materials can provide a high hydrogen storage density (30–100 kg/m³) in the future [7]. However, experimental studies in this area have shown that the sorption capacity of various carbon materials is less than 1 wt. % [10]. Therefore, many theoretical and experimental works have been carried out to find ways to increase the sorption capacity of carbon structures [11–20]. These works have demonstrated that reduction of the temperature and increasing of pressure have a very positive effect on the hydrogen storage by carbon structures. In experimental work [12], it was shown that at 77 K and a pressure of 1 atm. hydrogen sorption by graphene is 1.7 wt.%, while without applied pressure, the sorption of hydrogen by the same structure was less than 1 wt.% at 300 K [11]. Using the molecular dynamics (MD) method, it had been established that the gravimetric storage capacity of hydrogen inside pillared graphene bubble systems of different morphology can reach 13.0–13.7 wt.% at 77 K and 100 atm. [21].

In addition to external factors such as temperature and pressure, the sorption properties of carbon materials are also influenced by their structure, specific surface area, and the presence of defects. For instance, an increase in the specific surface area using an increase in the diameter or length of structural elements of carbon structures leads to an increase in their sorption properties [22]. The presence of defects in single-walled carbon nanotubes (CNT) increases the ability to accumulate hydrogen at room temperature [23, 24]. Ghosh et al. [25] reported that the doping of a single-walled carbon nanotube with Be atoms (especially if it is deposited

on the Stone-Wales defects) resulted in an increase in the gravimetric density of hydrogen up to 5.5 wt.% (bulk density 40 g·H₂/l) at room temperature and a pressure of 267 atm. Another important structural parameter for highly porous carbon systems is the size of the pores and voids into which hydrogen atoms and molecules can be stored: the pore size should be greater than 4.929 Å [26]. With a smaller pore size, the number of hydrogen molecules passing through them sharply decreases.

The experimental and theoretical works discussed above describe methods for improving the hydrogen sorption properties of various carbon structures. There are a large number of works devoted to the study of the hydrogenation and dehydrogenation processes of [27–29]. In these works, it is shown, that the adsorption of hydrogen atoms by the graphene surface leads to a change in the hybridization of carbon atoms from sp² to sp³. At the same time, the formation of ripples in layered graphene affects the binding energy between carbon and hydrogen atoms [30,31]. So the bonding energy formed between a hydrogen and a carbon atom inside the graphene ripple is lower than outside the ripple. These studies show that the adsorption properties of graphene depend on its morphology, and the more wrinkles and ripples in the structure of graphene, the higher its sorption properties should be.

The present work is focused on the study of the hydrogenation process of a crumpled graphene flake (CGF) in a hydrogen atmosphere. Graphene flake is a single element of crumpled graphene, which has a porous and complex wrinkled structure, due to which it shows good sorption properties. Using MD simulation, external factors (temperature and external hydrostatic pressure) are considered as having a positive effect on the hydrogenation process of a CGF. This work is a continuation of our earlier work [32], in which the dehydrogenation process of a single graphene flake was studied.

2. Simulation details

Figure 1a shows the simulation cell filled with hydrogen ($N_H=900$ atoms) with the CGF ($N_C=252$ atoms) placed in the center. The graphene flake is obtained by cutting out an atomic row from a carbon nanotube with a diameter 9.5 nm and a length 1.3 nm. The initial distance between hydrogen atoms is 8 Å, and the minimum distance between the GF and H is $l_0=3$ Å (see inset (I) in Fig. 1a) [33]. Such initial distances between atoms are chosen to exclude interactions between C-H and H-H atoms at the first modeling stage. The volume of the simulation cell is $80 \times 80 \times 80$ Å³.

To create a real atmosphere from an ideal hydrogen environment, i.e., consisting of randomly arranged H atoms and H₂ molecules, the initial structure in Fig. 1a is exposed at $T=300$ K for 20 ps. The structure after exposure is shown in Fig. 1b. It can be seen that as a result of exposure at room temperature, most of the separate H atoms transformed to H₂ molecules (see inset (II) in Fig. 1b). It should be noted that initially, the hydrogen atmosphere contained only atomic hydrogen. Also, during the temperature exposure, a certain amount of atomic hydrogen located near the carbon structure formed a CH group with edge carbon atoms (see inset (III) in Fig. 1b).

Note, that the first hydrogen molecules settle on the surface of CGF already in the thermal exposure process at 300 K. Some H₂ molecules, due to thermal fluctuations, approaching the flake plane at a distance less than 2.89 Å [13], settle on CGF interacting by van der Waals forces (see inset (III) in Fig. 1b).

The study of the sorption capacity of CGF in a hydrogen atmosphere is carried out under the influence of an applied external pressure p equal to 1 and 140 atm. at 77 and 300 K until the time moment at which the value of the hydrogen storage capacity became constant. The value of the applied pressure corresponds to those used to hydrogenate various carbon

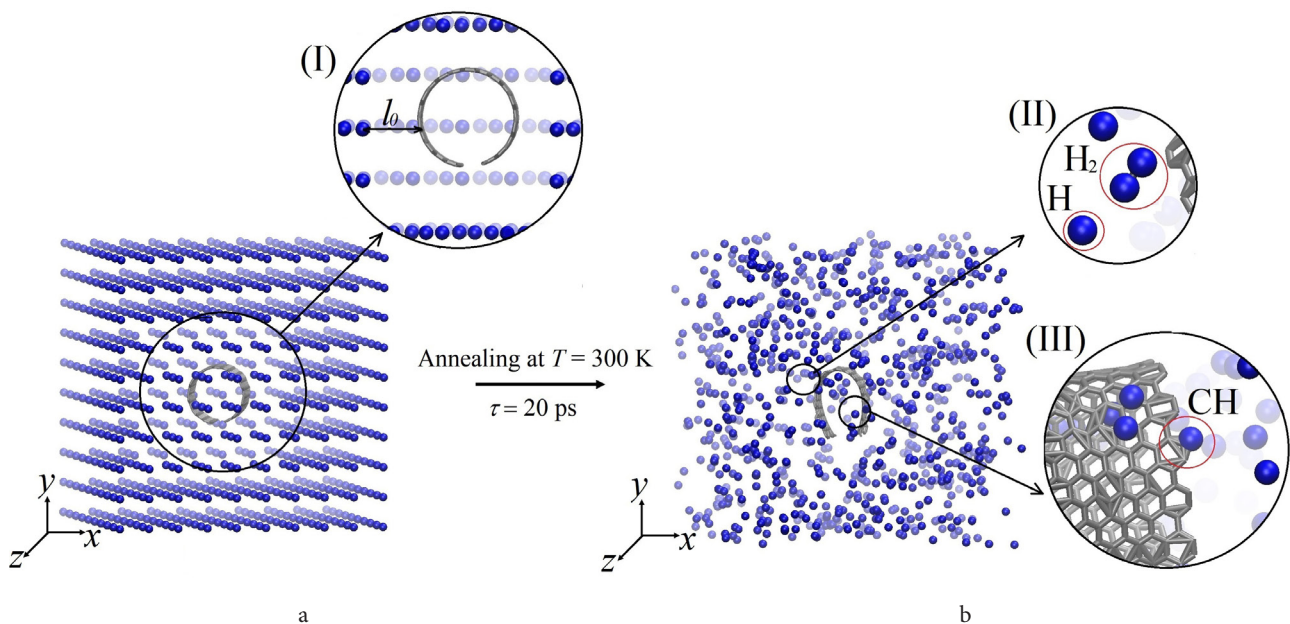


Fig. 1. (Color online) Schematic of a graphene flake in a hydrogen atmosphere: structure before (a) and after (b) exposure at $T=300$ K for 20 ps. Inset (I) shows graphene flake in higher magnification. The inset (II) shows the atomic hydrogen H and the H₂ molecule formed during the exposure, and the inset (III) shows the CH group in the edge of flake after exposure at 300 K. The CGF is shown by gray, and hydrogen atoms are blue.

structures [12]. The choice of hydrogenation temperatures is connected, firstly, with the best hydrogen sorption by carbon structures at 77 K (more than 2–3 wt.%), and secondly, with the requirement to achieve the optimal sorption capacity (more than 3 wt.%) at room temperature [34].

It should be noted that during simulation, the CGF edges are fixed in order to prevent the flake from opening under the influence of temperature. To do this, the *fix setforce* command is applied only to a carbon atoms group, which allows one to make the forces acting on each C atom at each simulation time equal to zero. This leads to the preservation of carbon atoms in their initial positions and does not affect the interaction of carbon atoms with hydrogen atoms.

The calculations were carried out using the freely distributed LAMMPS simulation package with the built-in AIREBO interatomic potential [35–39], which reproduces well the properties of various carbon-hydrogen structures [40].

During the simulation, periodic boundary conditions are set in all three directions. The equations of atomic motions are integrated numerically using the fourth-order Verlet method with a time step of 0.1 fs. To control the temperature during the simulation, a Nose-Hoover thermostat is used at all simulation stages. Temperature exposure at 300 K and the process of structure hydrogenation is carried out using the *NVT* and *NPT* ensemble (where *N* is the atomic number, *V* the volume, *T* the temperature and *P* is the pressure, which remain unchanged), respectively.

3. Results and discussion

In Fig. 2, the dependence of the gravimetric density (*g*) on time at *T*=77 K is shown. It can be seen that the gravimetric density of hydrogen increases almost monotonously with increasing of exposure time. At 1 atm., the value of *g* after *t*=70 ps reaches almost constant value until the end of exposure. The gravimetric density at 140 atm. reaches saturation at *t*>150 ps. From the snapshots of the CGF it is seen that atomic hydrogen adsorbs on the edges of the graphene flake. Molecular hydrogen settles on the surface of the CGF by of van der Waals interconnection. The higher the

external hydrostatic pressure, the more hydrogen atoms and molecules are absorbed by graphene. The maximum value of *g* is observed at a pressure of 140 atm. and is about 28 wt.%. Note that at a pressure of 1 atm. the gravimetric density of hydrogen reaches a constant value of 15 wt.%.

Figure 3 shows the change in the gravimetric density of a hydrogen during exposure at 300 K and two pressures. It can be seen, that at a higher applied pressure (140 atm.) *g* is higher. However, at exposure time longer than 10 ps, the gravimetric density is practically independent of the applied pressure. After 10 ps, hydrogen atoms begin to deposit intensively on the carbon structure under the influence of temperature and applied pressure. The subsequent wavy character of the *g(t)* curves (after holding for more than 20 ps in Fig. 3) is associated with the formation and destruction of van der Waals forces between hydrogen atoms and GFs. From the comparison of the snapshots of the CGFs in Fig. 3 it is seen that at 140 atm. the number of hydrogen atoms deposited on the flake edge is greater than at 1 atm. The gravimetric density at 1 atm. after exposure for 100 ps is about 7 wt.%, and at 140 atm. — about 10 wt.%. Note that at 300 K the number of hydrogen molecules and atoms inside the CGF is less than at 77 K. Thus, the gravimetric density at 300 K is 2.5 times less than at 77 K (at *p*=140 atm.).

In [40] it was shown by DFT that the maximum possible gravimetric density of carbon nanotubes (CNTs) is 7.7 wt.%. Our estimate of the gravimetric density of a crumpled graphene flake is more than 9 wt.%. Such a difference in *g* is due to the fact that in [41] only the physically adsorbed hydrogen inside a single-walled CNT was estimated. The presence of a large number of edge C atoms in the structure of a crumpled graphene flake leads to the absorption of hydrogen both by the surface of the flake and by edge C atoms, i.e. hydrogen adsorption (N_{ads}) by a CGF is divided into physical and chemical adsorptions, respectively. In the first case, hydrogen atoms settle on the graphene flake surface by the van der Waals forces. In the second case, the formation of strong covalent bonds between the edge carbon atoms and hydrogen atoms is observed. To analyze the contribution of chemical adsorption to the gravimetric hydrogen density

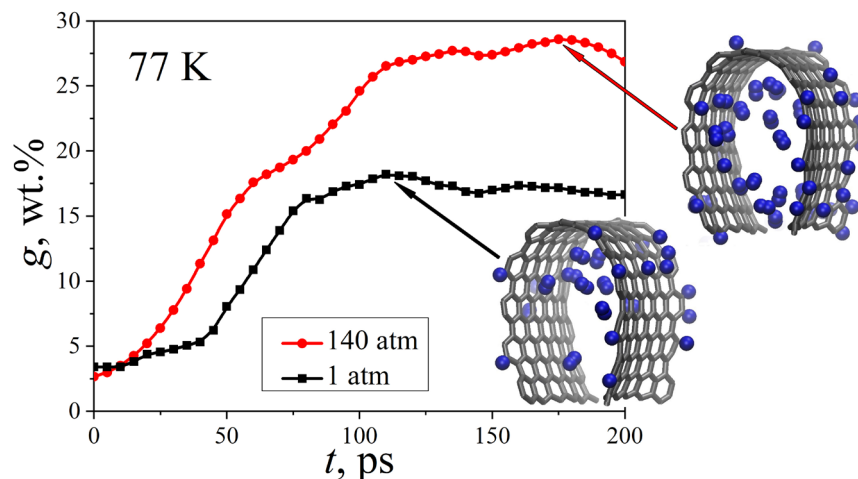


Fig. 2. (Color online) Gravimetric density as the function of exposure time and snapshots of CGF structures at 1 atm. (black curve) and 140 atm. (red curve). Exposure temperature is 77 K. The atoms colors are the same as in Fig. 1.

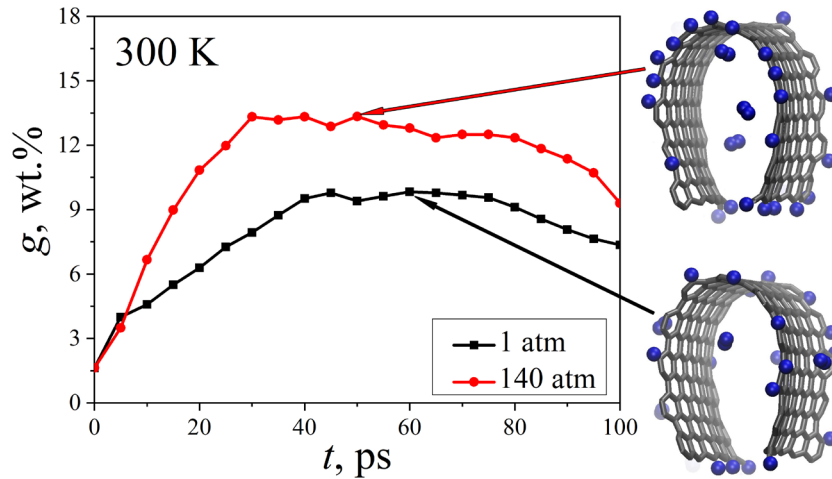


Fig. 3. (Color online) Gravimetric density as the function of exposure time at 1 atm. (black curve) and 140 atm. (red curve) and snapshots of CGF. Exposure temperature is 300 K. The atoms colors are the same as in Fig. 1.

of the studied CGF at two pressure and temperatures, the following formula is used:

$$n_{\text{ch}} = \frac{N_{\text{ch}}}{N_{\text{ads}}}, \quad (1)$$

where $N_{\text{ads}} = N_{\text{ph}} + N_{\text{ch}}$ is the number of all adsorbed atoms; N_{ph} corresponds to physical adsorption and N_{ch} to chemical adsorption. The number of adsorbed hydrogen atoms is estimated using own software packages that analyzed the bond length between hydrogen and carbon atoms. If the interatomic distances between the edge C atoms and H atoms is about 1.2 Å, then these are chemically adsorbed H atoms (N_{ch}). And if the bond length between hydrogen and carbon is from 3.0 to 3.3 Å, these are physically adsorbed H atoms (N_{ph}) [33].

Figure 4 shows the fraction of chemically adsorbed hydrogen atoms at two temperatures (77 and 300 K) and pressures (1 and 140 atm.) as the functions of the exposure time. It can be seen that at 77 K, the fraction of hydrogen atoms chemically adsorbed on the edge C atoms of the graphene flake is practically independent of the applied hydrostatic pressure and the exposure time. This suggests that the gravimetric density increases at this temperature only due to the atoms deposited on the graphene surface by means of van der Waals forces, i.e. physical adsorption prevails. The fraction of physically adsorbed hydrogen atoms at this temperature is more than 80%. At 300 K, the n_{ch} value, just as at 77 K, does not depend on the applied external pressure. However, with an increase in the exposure time at 300 K, the fraction of H atoms adsorbed on the edge C atoms increases to 0.8 and the proportion of n_{ch} becomes 4 times higher than at 77 K. This indicates that the chemical adsorption of hydrogen atoms of the graphene flake at 300 K prevails over the physical adsorption. The fraction of physically adsorbed hydrogen atoms is about 20% and mainly these are atoms deposited on the outer surface of crumpled graphene flakes. The external applied pressure does not affect the prevailing type of hydrogen adsorption at both studied temperatures.

It is known that at temperatures above $T_{\text{cr}} = 40$ K, the kinetic energy of H_2 molecules diffusing over the surface of the single-wall carbon nanotube (SWNT) bundle increases

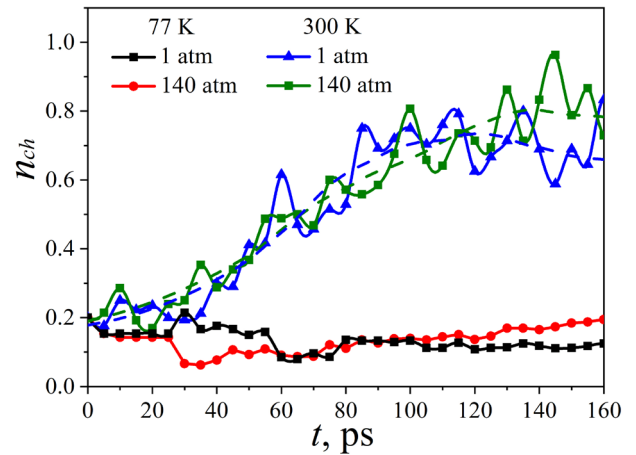


Fig. 4. (Color online) The relative fraction of chemically adsorbed hydrogen atoms at two temperatures (77 and 300 K) and pressure (1 and 140 atm.) as the function of exposure time. The dotted curves show the n_{ch} average value at 300 K.

[5]. As a result, hydrogen molecules quite easily leave the surface into the gaseous environment. In the present work, similar results are obtained, but for a flake of crumpled graphene. It is shown that when the hydrogenation temperature decreases from room temperature (300 K) to the boiling point of liquid nitrogen (77 K), the physical adsorption of a crumpled graphene flake at low temperatures becomes more difficult. This is due to a decrease in the kinetic energy of hydrogen atoms and molecules with a reduction in the temperature which becomes insufficient for the formation of strong covalent bonds between hydrogen atoms and edge carbon atoms, even if the atoms come to a sufficient distance from each other. However, as the temperature decreases, the chemical adsorption of hydrogen molecules increases, which leads to a rise in gravimetric density.

The external pressure is a factor that somewhat restrains the molecules and atoms of hydrogen in the carbon structure and hinders the movement of H_2 into the gas atmosphere. The pressure also increases the critical temperature (T_{cr}) at which the kinetic energy of hydrogen atoms reaches values that make it possible to destroy the weak van der Waals forces between H_2 molecules and carbon. As a result, the process

of gradual dehydrogenation of the carbon structure begins. Note that the chemisorption energy per hydrogen atom of a SWNT bundle changes from 1.775 to 1.452 eV depending on the number of nanotube layers in the bundle [33]. The approximate estimation of the chemical and physical adsorption energy at 77 K and 140 atm. is 1.4 and 0.03 eV, respectively. In our further work, we plan to evaluate the effect of temperature on the change in chemisorption energy per hydrogen atom of crumpled graphene and determine the T_{cr} of hydrogenation at different external pressures.

4. Conclusions

Using molecular dynamics simulation, it has been shown that the sorption capacity of a graphene flake placed in a hydrogen atmosphere is affected by the holding temperature and the magnitude of the applied pressure. The best hydrogen adsorption by a graphene flake is achieved at a combination of low temperature (77 K) and high pressure (140 atm.). However, it has been found that the gravimetric density value at 77 K is higher due to the physical adsorption of hydrogen atoms (the formation of weak van der Waals forces between the atoms and the surface of the CGF), while at 300 K the number of hydrogen atoms adsorbed by graphene flake increases mainly due to the chemical adsorption, which is associated with the formation of strong covalent bonds between edge carbon and hydrogen atoms. The external applied pressure affects the growth of the gravimetric density of the hydrogen, and the higher the pressure, the more H atoms are adsorbed by the structure. However, an increase in pressure has a greater effect on the increase in the physical adsorption of graphene than the chemical one.

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