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DEHYDROGENATION OF A CRUMPLED GRAPHENE FLAKE: MOLECULARDYNAMICS

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Abstract. Using molecular dynamics simulation, the dehydrogenation process of a crumpled graphene flake during annealing at 77, 100, 150, 200, 250, and 300 K for 200 ps is considered. It is found, that annealing at $T = 77$ K during the first 50 ps does not affect the gravimetric density. Further, exposure at this temperature results in a sharp decrease in the gravimetric density to 7.6 wt.%. It is found that the higher the temperature, the faster the dehydrogenation process of the carbon structure. At annealing temperatures above 150 K, the gravimetric density of crumpled graphene is set to a constant value, and an increase in the annealing time does not lead to a change of gravimetric density. This is because some of the hydrogen atoms remaining in the structure are deposited on the edge carbon atoms, forming a strong covalent bond that cannot be broken at such temperature.
Keywords: molecular dynamics, crumpled graphene, dehydrogenation

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1. Introduction

The search for new materials as a medium for storing and transporting hydrogen, as an alternative fuel,is currently underway. The U.S Department of Energy has established that the sorption capacity of the material for storing hydrogen must be at least 4.5 wt. % or 30 g H_2/liter by volumetric capacity at temperatures of 233 – 333 K [1].

Due to their high sorption capacity, carbon materials are promising media for hydrogen storage. However, studies have shown that the sorption capacity of various carbon materials is less than 1 wt.% [2]. Therefore, there were many theoretical and experimental works on the search for methods to increase the ability of carbon materials to adsorb hydrogen molecules [2-11]. One of the effective methods for improving the hydrogen sorption by carbon structures is hydrostatic compression and temperature reduction. In the experimental work [3], it was shown that the hydrogen sorption by graphene was 1.7 wt.% at a temperature of 77 K and a pressure of 1 atm. Without the application of hydrostatic pressure, the hydrogen sorption by this structure was less than 1 wt.% at 300 K [2]. With the help of molecular dynamics

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simulation, similar results were obtained [4,5].

One of the promising carbon structures as a medium for hydrogen storage was crumpled graphene (CG), due to its high porosity and high specific surface area (about 3523 m^2/g) [12-14]. The combination of these properties was associated with the peculiarity of the CG structure which is a mixture of crumpled graphene flakes of various shapes and sizes, connected by van der Waals forces [13].

In addition to hydrostatic compression and low temperature, the hydrogen sorption capacity was affected by the size of graphene flakes [15], as well as the defectiveness of structures [16,17], and many others. However, the dehydrogenation of carbon structures has been little studied [18]. However, understanding this process will lead to the emergence of new methods for improving the hydrogen sorption by carbon structures. Therefore, in this work, the dehydrogenation process of crumpled graphene flakes (CGF) at different temperatures is considered.

2. Simulation details

The initial structure of a single crumpled graphene flake is shown in Fig. 1(c). It is created based on a 1.35 nm long carbon nanotube (CNT) with chirality (11,11) (see Fig. 1(a)), which corresponds to CNT ~15 nm diameters (*D*). Along the zig-zag direction, 12 carbon atoms are cut out, forming an atomic row along the length of the CNT (the cut atoms were shown by a red rectangle in Fig. 1(a)). In the inner cavity of the obtained CGF, 78 hydrogen atoms are placed (see Fig. 1(b)). For clarity, hydrogen atoms are shown in Fig. 1(b and c) with a larger diameter than carbon atoms. With this position of H, the formation energy of the C-H bond will be the smallest [19]. The initial distance between the hydrogen and carbon atoms is more than 3.0 Å [7,20]. Hydrogen nanocluster diameter *d* is ~9 nm.

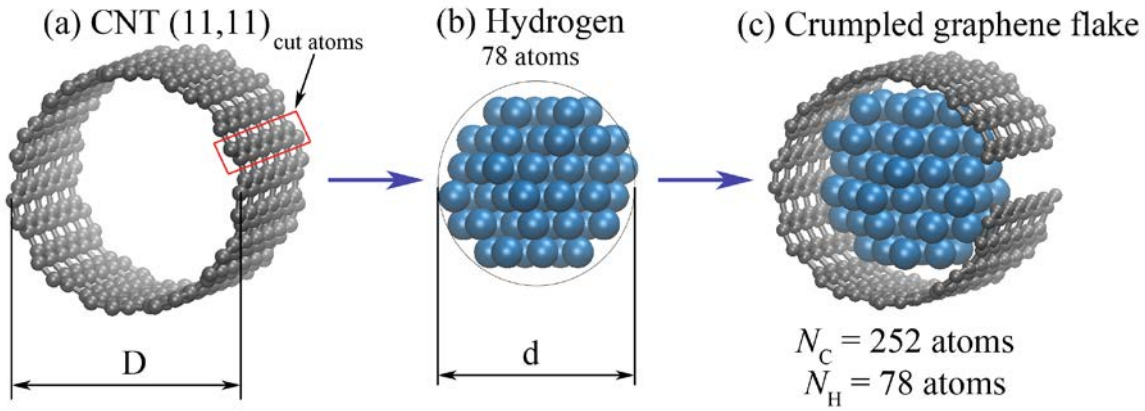

Fig. 1. (a) Structure of 1.35 nm long carbon nanotube (CNT) with $D \approx 15$ nm. The red rectangle marks the atoms to be cut out to create the flake. (b) A hydrogen nanocluster with a $d \approx 9$ nm. (c) The initial structure of a crumpled graphene flake. Carbon atoms are shown by gray and hydrogen atoms – by blue

The dehydrogenation process of the obtained structure is investigated at 77, 100, 150, 200, 250, and 300 K. A CGF is annealed at each temperature for 200 ps. The gravimetric hydrogen adsorption capacity (g [wt.%]) is calculated as

$$g = \frac{m_H}{m_H + m_c} \cdot 100, \quad (1)$$

where m_H is the mass of adsorbed hydrogen atoms, and m_C is the mass of carbon atoms. The amountof adsorbed hydrogen by the crumpled graphene structure is calculated using homemade software. Molecular dynamics simulation is carried out in the LAMMPS software package using the AIREBO interatomic potential [21]. With the help of this potential, many

problems on the properties of carbon [14,19,22-25] and carbon-hydrogen structures[4,5,18] were successfully solved. Periodic boundary conditions are applied in three directions *x*, *y*, and *z*. The temperature is controlled by the Nose–Hoover thermostat with NPT ensemble.

3. Results and discussion

The change in the gravimetric hydrogen adsorption capacity during annealing for 200 ps at different temperatures is shown in Fig. 2. It can be seen that the dehydrogenation process of the CGF occurs more slowly at low temperatures. Thus, annealing of a graphene flake at 77 K during the first 50 ps does not affect the value of the gravimetric capacity, but with further exposure, a sharp decrease in g is observed, and g = 7.6 wt.% at 200 ps. For an increase in the annealing temperature to 100 K, a sharp decrease in the gravimetric capacity is observed at t > 30 ps and g = 4.12 wt.% after exposure for 200 ps. A further increase in the annealing temperature leads to a sharp decrease in the gravimetric density at the first 10–20 ps to a constant value, which remains unchanged during the remaining annealing time.

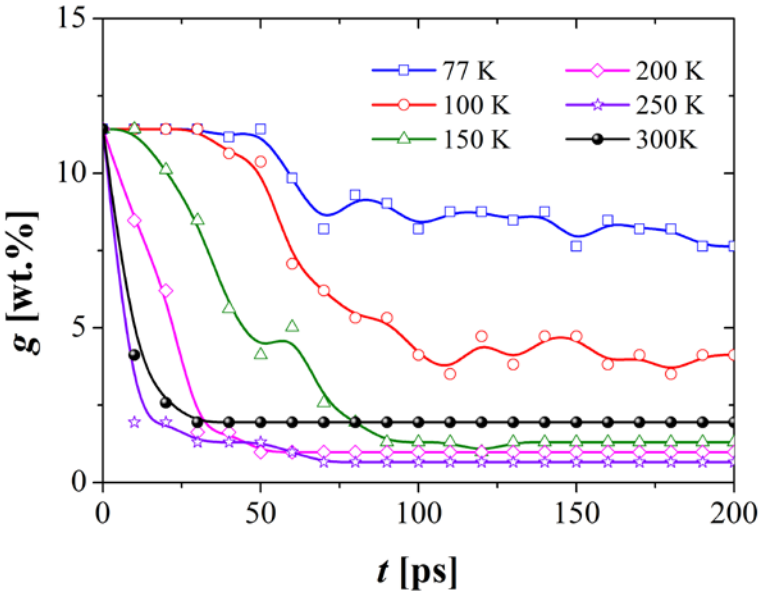

Fig. 2. Gravimetric hydrogen adsorption capacity at different temperatures as the function of time

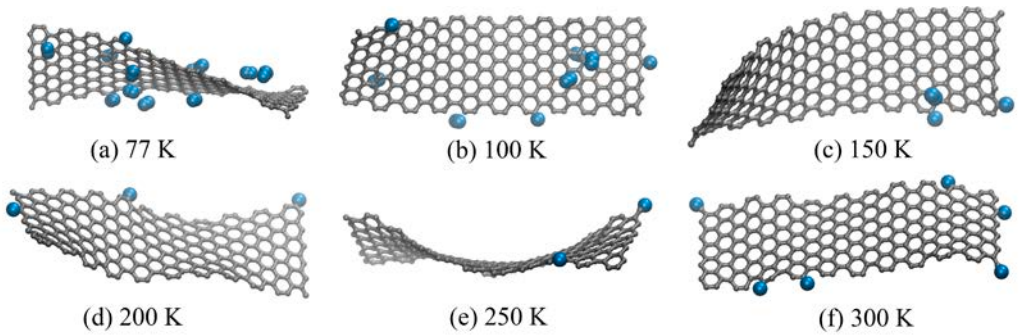

Fig. 3. Snapshots of the crumpled graphene flake after annealing at different temperatures for 200 ps. Carbon atoms are shown by gray and hydrogen atoms – by blue

Figure 3 shows the snapshots of the crumpled graphene flake after annealing for 200 ps. All CGFs are exposed at evaluated temperature for the first 5-10 ps, and the higher the temperature, the faster the flake opens. The opening of the graphene flake leads to a faster

dehydrogenation of the structure. Note that the introduction of Ni atoms into a graphene flake does not result in its opening under the action of even high temperatures (1000 K) [25].

At all considered temperatures, a hydrogen nanocluster decomposes into individual atoms, which transform into molecular hydrogen. H_2 is retained on the surface of crumpled graphene due to weak interatomic van der Waals forces, and under the action of thermal fluctuation migrates over the nanoflake surface. In Fig. 3(a and b), it can be seen that hydrogen is on both sides of graphene, although initially, it is only on one side (see Fig. 1).

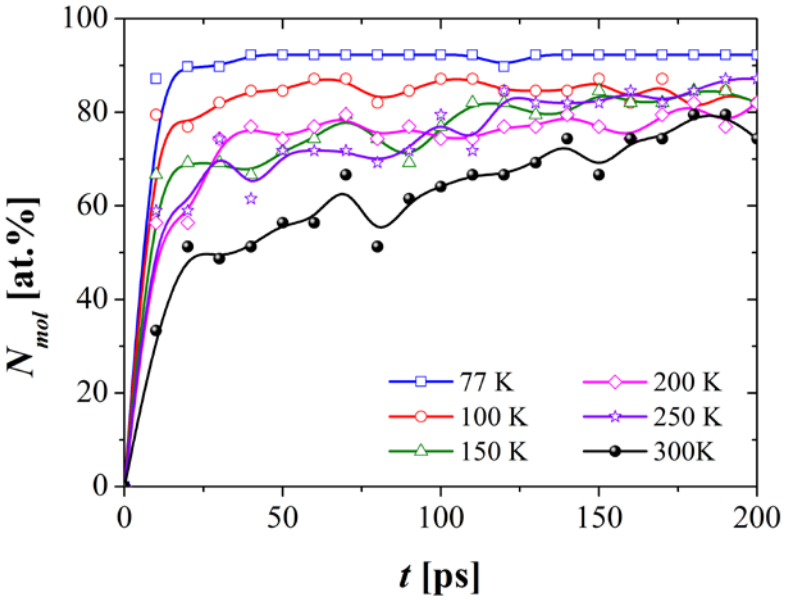

Fig. 4. Amount of molecular hydrogen N_{mol} at different temperatures as the function of time t.

The amount of molecular hydrogen (N_{mol}) is shown in Fig. 4, where it can be seen that at 77 K more90 at.% of hydrogen atoms form molecules, and this occurs during the first 10-20 ps of annealing. An increase in temperature leads to a smoother increase in the amount of molecular hydrogen in the structure. This is due to an increase in thermal vibrations of atoms in the structure with increasing temperature, which prevents the formation of new molecules. After annealing at 300 K for200 ps, more 70 at.% hydrogen formed molecules.

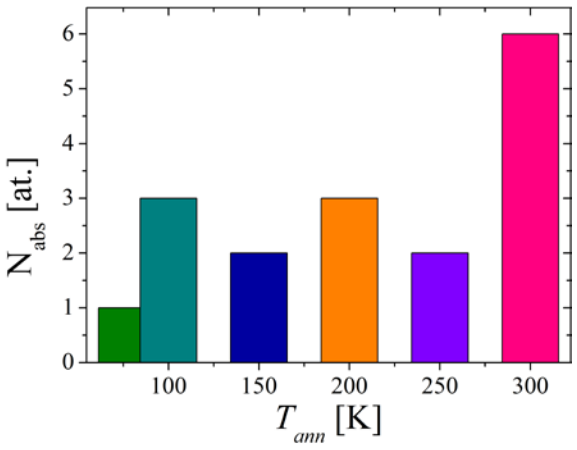

Fig. 5. Amount of absorbed hydrogen N_{abs} at the graphene flake edges at different temperatures

At annealing temperatures above 150 K, the gravimetric density of crumpled graphene is set at a constant value (see Fig. 2) and an increase in the annealing time does not lead to a change in g. This is because some hydrogen atoms, remaining in the structure, absorbed on

the edge graphene flake, forming CH group. The strong covalent bond formed between the carbon and hydrogen atoms cannot be destroyed at such a low temperature. Figure 5 shows the amount of absorbed hydrogen on edge carbon atoms at different temperatures after annealing for 200 ps. It can be seen that at T_{ann} = 300 K, the biggest number of absorbed hydrogen atoms is observed. Because at such a temperature the thermal fluctuations of hydrogen atoms are more intense, which results in a greater probability of the absorption of the H atoms to the edge C atoms. In addition, the amount of atomic hydrogen in the computational cell at 300 K is greater than at other annealing temperatures.

4. Conclusions

Molecular dynamics simulation made it possible to consider the process of hydration of crumpled graphene flakes at different annealing temperatures (from 77 to 300 K). The results obtained show that the best gravimetric density is achieved at 77 K. However, within 50 ps, a slight decrease in the sorption capacity of graphene is observed because not all hydrogen molecules have formed a van der Waals interaction with the crumpled graphene surface. But with further temperature exposure, the value of the gravimetric density remained practically unchanged. An increase in the annealing temperature above 150 K leads to rapid structure dehydration until a constant value is reached. The gravimetric density remained constant because the hydrogen atoms formed with the edge carbon atoms an interatomic CH group with a strong covalent bond that cannot be destroyed at these temperatures. The largest number of hydrogen atoms adsorbed on edge carbon atoms is observed at 300 K.

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