Effect of the structural elements size of crumpled graphene on hydrogen sorption: atomistic simulation

N G Apkadirova¹ and K A Krylova¹,²
¹Bashkir State University, 32 Z. Validy St., Ufa 450076, Russia
²Institute for Metals Superplasticity Problems of the Russian Academy of Sciences, 39 Khalturin st., Ufa 450001, Russia

E-mail: apkadirovanerkes@gmail.com

Abstract. The effect of the size of carbon flakes of crumpled graphene on the physical hydrogen sorption is considered using molecular dynamics simulation. Hydrogenated crumpled graphene was subjected to hydrostatic compression up to \( \varepsilon = 0.77 \), hydrogen dynamics in the dense structure is studied at 77 and 300 K. It has been found that the hydrogen sorption of crumpled graphene depends on its specific surface area. The highest sorption capacity was observed for crumpled graphene with carbon nanoflakes 20 nm in diameter. The difference in volumetric sorption capacity of flakes with the diameters of 9.5 and 20 nm was about 10% for a compression strain of \( \varepsilon = 0.77 \) at 20 ps at 77 K.

1. Introduction
Carbon materials are widely used in many industries due to their unique properties such as high strength, electrical and thermal conductivities, etc [1, 2]. In this connection, today a lot of theoretical and experimental studies are devoted to the investigation of such materials. 3D graphene-based materials, including crumpled graphene (CG), have a high specific surface area, porosity, and low weight [3, 4]. These properties open up the possibility of using such structures in hydrogen power engineering as a medium for hydrogen storing and transportation [5].

Many theoretical and experimental studies have shown that hydrogen sorption of CG can be increased due to a hydrostatic compression and a decrease in temperature [6, 7, 8]. In the experimental work [7], it was found that the hydrogen sorption of graphene is 1.7 wt.% under 1 atm. at 77 K, and it is less than 1 wt.% at 300 K but without compression [9]. A similar increase in the sorption capacity of CG was observed in theoretical studies using molecular dynamics simulation [6, 8, 10, 11, 12]. However, in addition to the above factors, the size of the structural elements of the CG can also affect the adsorption capacity, since the relative porosity of the structure changes by varying the diameter of the carbon nanoflakes constituent.

Thus, the possibility of increasing the hydrogen sorption of CG by changing the diameter of carbon nanoflakes formed from carbon nanotubes is investigated using molecular dynamics simulation.

2. Simulation details
The initial structure of CG with flakes of different diameters is shown in figure 1 (a) and (b). Carbon flakes were created based on 2.5 nm long carbon nanotubes with chirality (7,7) and (15,15), which corresponds to nanotubes 9.5 and 20 nm in diameters. According to the diameter of structural elements, we denote the studied structures of crumpled graphene - D\(_{9.5}\) and D\(_{20}\). The simulation cell contained...
3×3×3 graphene flakes (GFs) with a total number of atoms 13,770 (7,722 carbon atoms and 6,048 hydrogen atoms) and 26,649 (16,335 carbon atoms and 10,314 hydrogen atoms), in figure 1 (a) and (b), respectively. Atomic hydrogen was placed inside the GFs since in this case, the energy of the C-H bond will be lower [13] and, therefore, this bond is formed more easily. Note that increasing the size of the simulation cell does not affect the final simulation results.

To obtain a solid CG structure, hydrostatic compression at 0 K is used. Figure 1 (c) shows a change in the relative density $\rho/\rho_0$ (where $\rho_0$ is the initial density) of the CG structures with an increase of compression strain $\varepsilon$. The compressive strain of the CG was calculated from the change in the structure volume: $\varepsilon = (V_0 - V)/V_0$ (where $V_0$ is the initial volume). The maximum deformation of the $D_{9.5}$ and $D_{20}$ achieved using the AIREBO potential was estimated to be 77% and 83% respectively. In figure 1 (a) and (b), it can be seen that at $\varepsilon = 0.77$ a large number of pores is present that allows the structure to be compressed. In $D_{9.5}$, there are almost no pores, which complicates its further deformation. Note that further investigation of the hydration process of CG at 77 and 300 K was carried out at $\varepsilon = 0.0$ and 0.77.

![Figure 1](image.png)

Figure 1. Initial structure of crumpled graphene with structural elements 9.5 nm ($D_{9.5}$) (a) and 20 nm ($D_{20}$) in diameters (b) before and after hydrostatic compression ($\varepsilon = 0.77$). Graphene nanoflakes are black, hydrogen atoms are white. (c) Density-strain curves for hydrogenated $D_{9.5}$ (solid line) and $D_{20}$ (dashed line).

Molecular dynamics simulation is carried out using the publicly available and widely used LAMMPS package. To describe the interatomic interaction in CG, the adaptive intermolecular reactive empirical bond order (AIREBO) potential [14] was used. It was successfully applied in the study of deformation processes in 3D carbon structures [15, 16], as well as in the investigation of hydrogen sorption in these nanostructures [6]. After hydrostatic compression $D_{9.5}$ and $D_{20}$ structures are maintained at 77 and 300 K for 20 ps under the conditions of NVT ensemble with a Nose-Hoover thermostat.

3. Results and discussion

To compare the dehydrogenation process of the $D_{9.5}$ and $D_{20}$ structures annealed at 77 and 300 K for 20 ps, the change in the relative volumetric capacity of hydrogen $\rho V/\rho V_0$ (where $\rho V_0$ is the initial volumetric capacity of $H_2$) that leave the carbon structure was studied. Note that atomic hydrogen was placed in the initial structure of CG, but as a result of temperature exposure, most of the hydrogen was formed by $H_2$ molecules. Therefore, no chemical sorption of hydrogen by GFs is observed. However, the investigated carbon structure has good properties for the physical sorption of hydrogen, which is shown in this work.
In figure 2(a), the $\rho_V/\rho_{V0}(t)$ curves of hydrogenated $D_{9.5}$ and $D_{20}$ at $\varepsilon = 0.0$ and 0.77 are shown. It can be seen that up to 10 ps (dashed line in figure 2(a)), the diameter of GFs does not affect the sorption capacity of hydrogen at 77 K. However, for $t > 10$ ps, $\rho_V/\rho_{V0}(t)$ of $D_{9.5}$ continues to decrease monotonically, while for $D_{20}$ it is practically unchanged. The volumetric capacity of hydrogenated $D_{20}$ at 20 ps is 10% (15%) higher at $\varepsilon = 0.77$ (0.0) than $D_{9.5}$. Hydrostatic compression also affects the growth of the sorption capacity of CG [6], and it does not depend on the GFs diameter. Figure 2(b) shows the $D_{20}$ ($A$, $B$) and $D_{9.5}$ ($C$, $D$) structures after annealing at 77 K for 20 ps. In figure 2(b) $B$ and $D$, it can be seen that H$_2$ is deposited on the inside of the GFs due to Van-der-Waals forces, regardless of its diameter and degree of hydrostatic compression. However, the compressive deformation of the CG does not lead to the opening of the GFs, which affects the growth of the sorption capacity. The observed decrease in the volumetric capacity of hydrogen $D_{9.5}$ in comparison with $D_{20}$ is due to lower specific surface area of $D_{9.5}$ along with relatively high porosity.

Figure 2. (a) Relative volumetric capacity of hydrogenated $D_{9.5}$ and $D_{20}$ at 77 K for $\varepsilon = 0.0$ and 0.77 as the function of time. (b) Snapshots of the $D_{20}$ ($A$, $B$) and $D_{9.5}$ ($C$, $D$) structure for different values of strain after annealing at 77 K for 20 ps.

An increase in temperature has a negative effect on the sorption capacity of carbon structures (see figure 3(a) and (b)). A sharp decrease in $\rho_V/\rho_{V0}(t)$ at 300 K is observed, regardless of the GFs diameter and the degree of the compression of the structures. However, the dehydrogenation of $D_{9.5}$ occurs somewhat faster than that of $D_{20}$. Presumably, this is because the structure of $D_{9.5}$ is highly porous, which leads to the break of bonds between GFs (which can be observed in figure 3(b) $C$ and $D$). Note that the change in the volume hydrogen capacity after reaching the critical points $A$, $B$, and $C$, $D$ in figure 3(a) occurs in different ways. In compressed $D_{20}$, molecular hydrogen leaves the structure in large clusters (figure 3(a) $A$), which leads to an intense decrease in $\rho_V/\rho_{V0}$. Therefore, for $t > 3$ ps, $\rho_V/\rho_{V0}$ of the unstrained $D_{20}$ is higher than that of the deformed one. A similar effect is not observed in the $D_{9.5}$ structure and the release of hydrogen in this case occurs more uniformly. The rate of dehydrogenation of the unstrained structure is higher up to the critical points $C$ and $D$ in figure 3(b), where the amount of remaining hydrogen in the $D_{9.5}$ structure reaches the level of 0.16 and practically does not change during further annealing at 300 K. The deposition of hydrogen molecules on GFs during annealing at 300 K is not observed, since thermal fluttering destroys weak Van-der-Waals forces between hydrogen and carbon atoms, this is the main reason for the dehydrogenation of CG.
Table 1 summarises the data on the number of hydrogen atoms $N_{\text{out}}$ (%) released from the structures of $D_{9.5}$ and $D_{20}$ at different strains ($\varepsilon = 0.0, 0.77$) after temperature exposure at 77 and 300 K for 20 ps. It can be seen that hydrostatic compression leads to a decrease in the number of hydrogen released from the structure at 77 K. Thus, after annealing for 20 ps, about 5% of H atoms moved out the structure of the $D_{20}$ at $\varepsilon = 0.77$, which is almost 4 times less than $N_{\text{out}}$ of the undeformed $D_{20}$. However, raising the annealing temperature to 300 K significantly increases the dehydrogenation of structures. The smaller is the diameter of the GFs and the greater is the degree of its compression, the more hydrogen will be released from it. This is primarily due to the destruction of the Van-der-Waals forces between atoms due to thermal fluctuations.

### Table 1. Number of hydrogen atoms $N_{\text{out}}$ (%) moved out from the CGs structures at $\varepsilon = 0.0$ and $\varepsilon = 0.77$ after annealing at 77 and 300 K for 20 ps.

| CG type | 77 K $\varepsilon = 0.0$ | 77 K $\varepsilon = 0.77$ | 300 K $\varepsilon = 0.0$ | 300 K $\varepsilon = 0.77$ |
|---------|------------------------|------------------------|------------------------|------------------------|
| $D_{9.5}$ | 56.63 | 43.75 | 88.76 | 89.38 |
| $D_{20}$ | 20.97 | 5.26 | 59.12 | 75.50 |

4. Conclusions

Using molecular dynamics simulation it is found that the sorption capacity of crumpled graphene depends on the geometric size (diameter of graphene flakes) of its structural elements. Larger the specific surface area of the crumpled graphene flakes (i.e., the larger the radius of the GFs), the higher its physical sorption. The volumetric capacity of hydrogen $D_{20}$ at $\varepsilon = 0.77$ and holding at 77 K was 10% higher than that of $D_{9.5}$ under the same conditions. Hydrostatic compression of the CG structure also leads to a significant increase in the physical sorption of hydrogen. Thus, the number of hydrogen atoms released from the deformed $D_{20}$ structure ($\varepsilon = 0.77$) after annealing at 77 K for 20 ps is 4 times lower than that of the undeformed $D_{20}$ under the same conditions.

The data obtained significantly expand the understanding of the application of carbon structures for hydrogen storage and transportation. By varying the size of the structural elements of crumpled graphene and its temperature-deformed state, one can increase the sorption capacity of such structures. And by increasing the temperature from 77 to 300 K, molecular hydrogen can be released for further use.
Acknowledgments
The work was supported by the State Assignment of IMSP RAS.

References
[1] Safina L, Baimova J, Krylova K, Murzaev R and Mulyukov R 2020 Letters on Materials 10 351–60
[2] Dmitriev S V 2016 Letters on Materials 6 86–9
[3] Zhang L, Zhang F, Yang X, Long G, Wu Y, Zhang T, Leng K, Huang Y, Ma Y, Yu A and Chen Y 2013 Scientific Reports 3 1408
[4] Baimova J A, Liu B, Dmitriev S V and Zhou K 2015 Journal of Physics D 48 095302
[5] Broom D, Webb C, Fanourgakis G, Froudakis G, Trikalitis P and Hirscher M 2019 International Journal of Hydrogen Energy 44 7768–79
[6] Krylova K A, Baimova J A, Lobzenko I P and Rudskoy A I 2020 Physica B 583 412020
[7] Ghosh A, Subrahmanyam K S, Krishna K S, Datta S, Govindaraj A, Pati S K and Rao C N R 2008 The Journal of Physical Chemistry C 112 15704–07
[8] Krylova K, Baimova J and Mulyukov R 2019 Letters on Materials 9 81–5
[9] Ritschel M, Uhlemann M, Gutfleisch O, Leonhardt A, Graff A, Täschner C and Fink J 2002 Applied Physics Letters 80 2985–7
[10] Katin K P, Prudkovskiy V S and Maslov M M 2017 Physics Letters A 381 2686–90
[11] Krasnov P O, Shkaberina G S, Kuzubov A A and Kovaleva E A 2017 Applied Surface Science 416 766–71
[12] Pei Q X, Sha Z D and Zhang Y W 2011 Carbon 49 4752–59
[13] Lobzenko I, Baimova J and Krylova K 2020 Chemical Physics 530 110608
[14] Stuart S J, Tutein A B and Harrison J A 2000 The Journal of Chemical Physics 112 6472–86
[15] Baimova J A, Rysaeva L K, Liu B, Dmitriev S V and Zhou K 2015 Physica status solidi (b) 252 1502–7
[16] Baimova Y A, Murzaev R T and Dmitriev S V 2014 Physics of the Solid State 56 2010–16