



## <sup>4</sup>He Sorption in Graphene Oxide at Low Temperatures

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The sorption and subsequent desorption of <sup>4</sup>He gas by grapheme oxide (GO) and hydrazine-reduced grapheme oxide (RGO-Hz) powders have been investigated in the temperature interval 2 – 25 K. It is found that the Hz-reduction of GO increases the sorptive capacitance of RGO-Hz by a factor of 3.3 in comparison with GO. It is assumed that the sorptive capacity of the RGO-Hz sample increases because the O<sub>2</sub>-containing groups are removed in the process of Hz-reduction of GO, which makes the interlayer space accessible for sorption

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### 1. INTRODUCTION

Oxidation of graphite and the subsequent ultrasonic dispersion of the graphite oxide to the state of graphene oxide (GO) is one of the simple technologies of large-scale production of graphene-based materials [1]. Graphene oxide consists of intact graphite areas with inclusions of sp<sup>3</sup>-hybridized carbon atoms. The inclusions contain hydroxyl and epoxy functional groups at the upper and bottom surfaces of every graphene sheet and sp<sup>2</sup>-hybridized carbon containing carboxyl and carbonyl groups located mainly at the edges of the graphene sheet.

Graphene oxide, like graphite, has a layered structure consisting normally of several graphene layers. The layer spacing vary within 6-8 Å depending on the technology of GO preparation and the oxidation level [2, 3]. The carbon layers of GO are deformed by the sp<sup>2</sup> → sp<sup>3</sup> transitions of the C atoms. Normally, GO contains a great number of topological structural defects and ruptures. The GO layers are weakly related to each other.

The O<sub>2</sub> – containing groups can be removed partially by reducing graphene oxide, for example, with hydrazine, dimethyl hydrazine, hydroquinone, sodium boron hydride and so on. It is however essential that the residual oxide groups and the surface defects inevitable in the process of GO reduction affect seriously the structure of the graphene plane. This suggests that reduced graphene oxide (RGO) and graphene can hardly be taken as completely similar substances. The RGO technology is one of the methods used to produce macroscopic quantities of a graphene –like material for wide – range applications.

Owing to their large specific area of surface [4, 5], GO and RGO can be used as high – efficiency sorbents.

In this context investigations of the sorptive characteristics of GO and RGO reactive toward a helium impurity at low temperatures rank among the urgent research problems, especially for the use of GO in cryogenic engineering.

### 2. EXPERIMENTAL TECHNIQUE

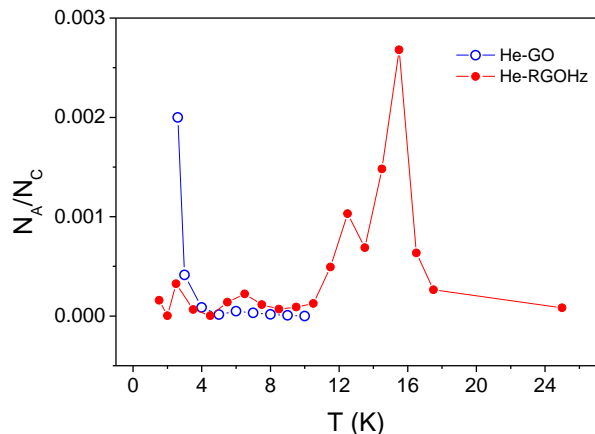
The sorptive properties and the saturation-desorption kinetics of He impurity in graphene oxide (GO) and hydrazine – reduced graphene oxide (RGO-Hz) have been investigated experimentally using a laboratory stand (its design and operation are detailed in [6, 7]). The temperature interval was 2-25 K. The GO and RGO-Hz samples were powders with ~ 10 μm grains and masses of ~40 mg. Immediately before starting the investigation, the powder samples were evacuated for five days at room temperature in the measuring cell of the stand to remove the possibly available gas impurities and moisture.

The pressure of GO saturation with each impurity was ~ 1 Torr. As soon as the sample absorbed the gas, a new portion of impurity was added to the cell. The saturation temperature was chosen so that the pressure of the gas impurity in the measuring cell remained in the process of saturation 2.5 – 3 times lower than the saturation vapor pressure of the impurity at this temperature. These sorption condition excluded condensation of the impurity vapors and the formation of films at the grain surfaces and the cell walls. Feeding the gas impurity was stopped when the equilibrium pressure 10<sup>-2</sup> Torr was achieved in the cell. The cell was then sealed and the changes in the pressure were recorded in the process of impurity desorption from the powder on its stepwise heating. The gas impurity evolved due to the heating was taken to an evacuated calibrated vessel. The pressure in it was measured with two capacitance manometer (MKS-627B) capable of measuring pressure in the range 10<sup>-3</sup> – 1000 Torr, the error being 1·10<sup>-4</sup> Torr. When the pressure was stabilized, the vessel was detached from the sample, evacuated and then joined to it again. The gas extraction was continued until the gas pressure over the sample reduced to 10<sup>-2</sup> Torr. Then the measurement was repeated at the next value of temperature.

### 3. RESULTS AND DISCUSSION

The temperature dependences of the quantities of

$^4\text{He}$  gas desorbed from the GO and RGO-Hz samples are illustrated in Fig.1. The number of impurity particles  $N_A$  is normalized to the total number  $N_C$  of C atoms in the samples. Note that the total quantities of the sorbed and desorbed impurities coincide within the experimental error.



**Fig. 1** – The temperature dependences of the relative quantity of  $^4\text{He}$  impurity desorbed from the GO and RGO-Hz samples.

The total concentrations of the  $^4\text{He}$  impurity atoms in the GO and RGO-Hz samples were 0.0026 and 0.00867, respectively (in molar fractions, i.e. the number of impurity particles per C atom).

It is seen in Fig.1 that the temperature intervals of the dominant bulk of  $^4\text{He}$  desorption are different for the GO and RGO-Hz samples. This may be due to the features of the sample structures. It is probable that the access of the impurity particles to the interplanar space of GO is limited by the oxide groups. As a result, the

sorption of impurities proceeds mainly at the outer surfaces of the grapheme planes. The Hz-reduction reduces the distance between the layers to 0.55 nm [8] or even 0.44 nm when the epoxy and hydroxyl groups are nearly fully removed from both sides of the grapheme plane [9]. The Hz-reduction of GO changes drastically the character of the desorption curves by shifting the desorption maximum towards higher temperatures for all of the investigated impurities. Most likely the Hz-reduction of GO is an efficient way of removing the functional groups which block the access to the space between the grapheme planes. Since the impurity particles in the interplanar space of the RGO-Hz sample have higher binding energies than those at the outer grapheme surface [10], the particle desorption from the interplanar space proceeds at a higher temperature. The assumption of a greater possibility for sorption in the interplanar space of the RGO-Hz sample is supported by the higher (3.3 times) sorptive capacity of this sample in comparison with the GO one.

#### 4. CONCLUSIONS

The sorption and the subsequent desorption of  $^4\text{He}$  gas by the powders of grapheme oxide (GO) and hydrazine – reduced grapheme oxide (RGO-Hz) have been investigated in the temperature interval 2-25K. It has been found that Hz-reduction of GO causes significant changes in the sorptive properties: the total sorptive capacity of the RGO-Hz sample is 3.3 times higher than that of the GO sample. The increase is most likely due to removal of oxygen-containing groups in the Hz-reduction of GO, which makes the interplanar space of GO accessible for sorption.

#### REFERENCES

1. S. Mao, H. Pu and J. Chen, *RSC Advances* **2**, 2643, (2012).
2. A. B. Bourlinos, D. Gournis, D. Petridis, T. Szabo, A. Szeri, I. Dekany, *Langmuir* **19**, 6050 (2003).
3. M. Hirata, T. Gotou, S. Horiuchi, M. Fujiwara, M. Ohba, *Carbon* **42**, 2929 (2004).
4. G. Srinivas, J. Burres, T. Yildirim, *Energy Environ. Sci.* **5**, 6453 (2012).
5. G. Srinivas, J. W. Burrell, J. Ford, T. Yildirim, *J. Mater. Chem.* **21**, 11323 (2011).
6. A.V. Dolbin, V.B. Esel'son, V.G. Gavrilko, V.G. Manzhelii, N.A. Vinnikov, S.N. Popov, *JETP Lett.* **93**, 577 (2011).
7. A.V. Dolbin, V. B. Esel'son, V. G. Gavrilko, V. G. Manzhelii, N. A. Vinnikov and S. N. Popov, *Fiz. Nizk. Temp.* **36**, 1352 (2010) [*Low Temp. Phys.* **36**, 1091 (2010)].
8. O. Akhavan, E. Ghaderi, S. Aghayee, Y. Fereydooni, A. Talebi, *J. Mater. Chem.* **22**, 13773 (2012).
9. M.X. McAllister, J.L. Li, D.H. Adamson, H.C. Schniepp, A.A. Abdala, J. Liu, M. Herrera-Alonso, D.L. Milius, R. Car, R.K. Prud'homme, I.A. Aksay, *Chem. Mater.* **19**, 4396 (2007).
10. V. Tozzini, V. Pellegrini, *Phys. Chem. Chem. Phys.* **15**, 80 (2013).