JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. 7 No 2, 02008(3pp) (2015)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том 7 № 2, 02008(3cc) (2015)

The Effect of Reduction Temperature of Graphene Oxide on Low Temperature Hydrogen Sorption

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(Received 02 April 2015; published online 10 June 2015)

Sorption and subsequent desorption of hydrogen by graphene oxide powder which was thermally reduced at temperatures of 200, 300, 500, 700 and 900 °C were investigated in 9-290 K temperature interval. The resulting dependence of the quantity of adsorbed hydrogen on the reduction temperature had a non-monotonic character. The maximum values of the quantity of sorbed hydrogen were observed for the samples reduced at temperatures of 300 and 900 °C. It was assumed that the increase in the sorption ability of the samples reduced at 300 °C is due to the disordering of the layered structure of graphene oxide by removing the intercalated water. Heat treatment at 900 °C also increased the sorption capacity of the sample due to the formation of multiple defects of carbon surfaces by removing oxygen-containing groups.

Keywords: Graphene oxide, Thermal reduction, Hydrogen sorption.

PACS numbers: 68.43.Jk, 68.43.Mn

1. INTRODUCTION

Graphene is a single-layer two-dimensional carbon structure, whose surface consists of regular hexagons with a side of 1.42 Å [1], and sp^2-hybridization carbon atoms are at each vertex. Such a structure is a component of crystalline graphite, in which these graphene planes are spaced apart at a distance approximately equal to 3.35 Å [1]. Interest in the production, investigation and practical application of graphene was extremely increased after discovery of a relatively simple method for separation of an individual graphene sample and formation of macroscopic materials based on graphene (graphene oxide, graphene-oxide paper). This interest is related to unique physical and chemical properties of graphene: high electrical [2] and thermal [3] conductivity, dependence of the electronic characteristics on the presence of attached radicals of different nature on the surface of graphene [4], adjustable bad gap [5], quantum Hall effect [6], extremely high mobility of charge carriers [7], high elasticity. The specified properties are attractive from the point of view of possible applied use of graphene as the basis for new nanomaterials with improved mechanical, electrical and thermal and physical characteristics as well as high-efficient gas [8, 9] and biological [10, 11] sensors.

Graphene oxide consists of undamaged graphite areas with inclusions of *sp*^{3}-hybridized carbon atoms which contain hydroxyl and epoxy functional groups on the upper and lower surfaces of each graphene sheet as well as of *sp*^{2}-hydridized carbon containing carboxyl and carbonyl groups mainly concentrated on the edges of a graphene sheet. Similarly to graphite, graphene oxide has a layered structure (it usually consists of some carbon layers). Distance between neighboring layers is approximately equal to 6-8 Å [12, 13] (depending on the way of production of graphene oxide and degree of its oxidation). Carbon layers in graphene oxide are strained because of the transition of carbon atoms from *sp*^{2} into *sp*^{3}-hybridized state. Graphene oxide usually has a large amount of topological structural defects and discontinuities. Layers of graphene oxide are weakly coupled with each other.

Thermal reduction is currently one of the widely used methods for production of graphene-like materials in the industrial scale. Thermally reduced graphene oxide (TRGO) is obtained from graphene-oxide (GO) [14, 15], which, in turn, is produced from graphite using different chemical oxidizers [13, 16]. Thermal reduction of graphene is of interest not only due to the substantial decrease in the cost of mass production of graphene, but also because of the absence of chemical reducing agents. Traces of chemical reducing agents cannot be completely removed from the graphene oxide powder or film [17-19] that makes it ineligible for a number of biological and medical applications. It should be kept in mind that residual oxide groups as well as surface defects inevitably arising in the reduction of graphene oxide significantly change structure of a graphene plane, and as a result it is impossible to make a complete comparison between reduced graphene oxide (RGO) and graphene. Thermal reduction of graphene oxide is a rather complex process because of thermally activated multistage removal of intercalated water molecules and oxide groups, such as carboxyl (−COOH), carboxyl and partly hydroxyl (C−OH and O−H), epoxy (C–O–C), singly connected on the surface oxygen (C–O), and carbonyls (C=O).

Presence of water and oxygen-containing groups very strongly influences the physical properties of graphene oxide including its sorption characteristics. Graphene oxide and reduced graphene oxide, due to their high specific surface area [20, 21], are used as high-efficient sorbents. From this point of view, the study of sorption characteristics of GO and RGO in a wide temperature range, especially for hydrogen applied in modern energetics, is actual.

2. DESCRIPTION OF THE OBJECT AND METHOD OF STUDY

Sorption characteristics of graphene oxide with respect to molecular hydrogen depending on the thermal reduction temperature of graphene oxide were studied in the given work. The initial graphite oxide (GtO) was obtained by the modified Hummers method from graphite powder. Subsequent reduction and exfoliation of graphene oxide were performed by thermal heating of GtO in argon atmosphere. Five samples, each of which during reduction was heated to a certain maximum temperature of 200, 300, 500, 700, and 900 °C, were subjected to processing. Sorption properties of thermally reduced samples of graphene oxide were studied using laboratory bench, the design and operating principle of which were described earlier in detail [22, 23]. Investigations were performed in the temperature range of 9-290 °K. Prior to the study, powder samples, for the purpose of removal of possible gaseous impurities and moisture, were evacuated during five days at room temperature directly in the measuring cell of the bench.

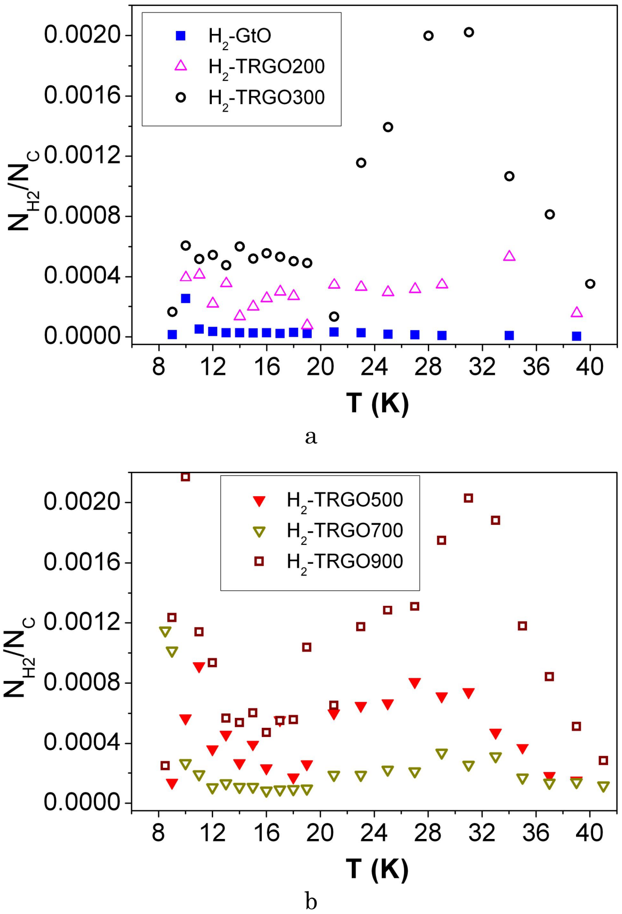
Saturation of GtO and thermally reduced samples of graphene oxide with hydrogen was carried out at the pressures of ~ 1 torr. The minimum temperature of the study was conditioned by the gaseous hydrogen pressure in the measuring system, which during saturation was maintained 2.5-3 times less than the equilibrium H_2 saturated vapor pressure at the current temperature. With hydrogen sorption by the sample, additional portions of gas were added into the cell. Such saturation mode of the samples allowed to avoid condensation of hydrogen vapor and formation of a film on the surface of powder grains and cell walls. Supply of gaseous H_2 was ceased when equilibrium pressure of 10^{-2} torr was achieved in the cell. Then, the cell was encapsulated, and pressure change during hydrogen desorption from powder at stepwise heating was registered. Gaseous hydrogen extracted during heating was taken into evacuated calibrated volume, in which pressure was measured using two capacitive pressure sensors MKS-627 allowing to measure pressures from 10^{-3} torr to 1000 torr to an accuracy of $\pm 1{\cdot}10^{-4}$ torr. Gas off-take from the samples lasted till gas pressure above the sample decreased to 10^{-2} torr, after that the transition to the successive temperature value was performed.

3. DESCRIPTION AND ANALYSIS OF THE RESULTS

Temperature dependences of the amount of hydrogen desorbed from the samples of GtO and thermally reduced graphene oxide are represented in Fig. 1.

Control of desorption was carried out in the temperature range of 9-290 K, however, almost all adsorbed hydrogen was desorbed from the samples at heating to 40 K. Dependence of the total amount of desorbed hydrogen on the reduction temperature of the sample is given in Fig. 2 and Table 1. In Fig. 1 and Fig. 2 as well as in Table 1, amount of desorbed hydrogen molecules N_{H2} is normalized to the total amount of carbon atoms in N_C samples.

We note that total amounts of adsorbed and desorbed by the sample hydrogen within the experimental error coincided. The obtained dependence between reduction temperature of the sample and total amount of adsorbed hydrogen has a non-monotonic behavior with the maximum values of adsorbed hydrogen for the samples reduced at 300 and 900 °C (Fig. 2). Increase in the sorption ability of the sample at heating to 300 °C, appearingly, is explained by the disorder of the GtO layered structure at evaporation of intercalated water. Heating to 700 °C induces removal of oxygen-containing groups, defect formation, and decrease in the distance between



a

b

Fig. 1 – Temperature dependences of the relative amount of hydrogen desorbed from the samples: a – GtO (■), TRGO reduced at 200 °C (Δ), 300 °C (○); b – TRGO reduced at 500 °C (▼), 700 °C (▽) and 900 °C (□)

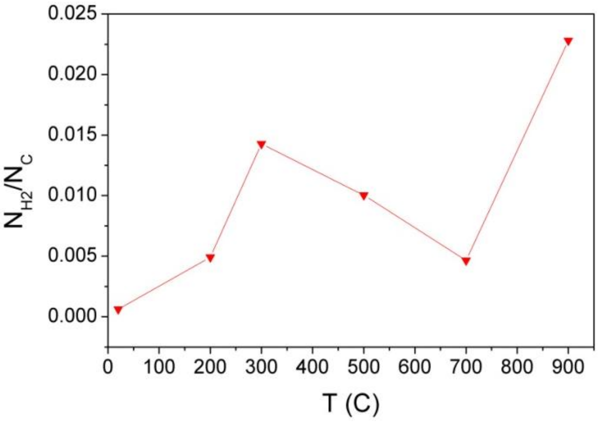


Fig. 2 – Dependence of the relative amount of adsorbed hydrogen on the reduction temperature of the sample

Table 1 – Total concentrations of hydrogen in GtO and TRGO samples at different reduction temperatures (in mole fractions (the number of hydrogen molecules per one carbon atom) and mass percent)

Sample	GtO	TRGO-200	TRGO-300	TRGO-500	TRGO-700	TRGO-900
N_{H2} / N_C	0.00061	0.005	0.014	0.010	0.0047	0.023
wt. %	0.01	0.08	0.23	0.17	0.08	0.38

the layers of graphene that reduces the sorption capacity of the samples.

Heat treatment at higher temperature (900 °C) can lead to removal of residual oxygen-containing groups and formation of a large amount of defects [24] that makes interlayer spacing of graphene oxide available for sorption and increases the sorption capacity of the sample. Generation of multiple defects of carbon planes with increasing reduction temperature is accompanied by the appearance of expressed second desorption maximum at the temperature of about 10 K (Fig. 1b, samples TRGO-500, TRGO-700, and TRGO-900).

4. CONCLUSIONS

Desorption spectra characterizing the sorption capacity of the samples of thermally reduced graphene oxide with respect to hydrogen in the temperature range of 9-40 K were obtained by the method of thermal programmed desorption. Dependence of the amount of desorbed hydrogen on the reduction temperature of the samples was graphically plotted based on the experimental data. It was assumed that thermal reduction of GtO by heating in the argon environment to 300 °C leads to evaporation of water intercalated between carbon layers that induces exfoliation of graphene planes and increase in the sorption capacity. Thermal reduction at heating to 700 °C decreases the sorption capacity of graphene oxide because of the removal of oxygen-containing groups and decrease in the distance between the layers of graphene. Heating of the sample to 900 °C causes the appearance of multiple defects of carbon planes that opens the interlayer spacing for sorption and increases the sorption capacity.

ACKNOWLEDGEMENTS

The authors of the paper express their gratitude to M.I. Bagatskii for the fruitful discussions.

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