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INVESTIGATION OF TEMPERATURE INFLUENCE ON THE PROCESS OF REDUCTION OF GRAPHENE OXIDE

The paper presents the results of influence different temperature on reducing graphene oxide. The influence of atmosphere pressure hydrogen gas at temperatures: 150 °C, 300 °C, 500 °C, 900 °C on the structure and composition of functionalized graphene was studied. The positions and ratio of Raman peaks of graphene oxide and thermally-reduced graphene are shown. Collected SEM images of graphene oxide are demonstrates layered structure, and the elemental composition of the thermally-reduced graphene at various temperatures was determined by using EDX spectroscopy. The obtained elemental analysis results are in good agreement with the data on the mass loss of thermally-reduced graphene, which is explained by the removal of functional groups.

Key words: graphene, graphene oxide, reduced graphene oxide, Raman spectroscopy, energy dispersive x-ray spectroscopy, energy dispersive analysis.

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Графен оксидін қалпына келтіру үрдісіне температураның әсерін зерттеу

Бұл мақалада графен оксидін қалпына келтіру бойынша нәтижелер көрсетілген. Сутекті атмосферадағы: 150 °C, 300 °C, 500 °C, 900 °C температуралардың функцияландырылған графеннің құрылымы және құрылысына әсер етуі анықталған. Графен оксидінің және температуралы қалпына келтірілген графен Раман пиктерінің деңгейі мен қатынасы көрсетілген. Сканерлеуші электронды микроскопта микрофотографиялар түсірілген, сонымен қатар ЭДС әдісі арқылы әр түрлі температурадағы температуралы қалпына келтірілген графеннің элементтік құрылымы анықталды. Элементтік талдаудан алынған нәтижелер температуралы қалпына келтірілген графен массасының жоғалтуындағы мәліметтермен сәйкес келуі функционалды топтардың жоюылуын түсіндіреді.

Түйін сөздер: графен, графен оксиді, температуралы қалпына келтірілген графен, Раман спектроскопиясы, энергия-дисперсиялық рентген спектроскопиясы, энергия-дисперсиялық талдау.

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Исследование влияния температуры на процесс восстановления оксида графена

В данной работе представлены результаты по восстановлению оксида графена. Было изучено влияние температур: 150 °C, 300 °C, 500 °C, 900 °C в атмосфере водорода на структуру и состав функционализированного графена. Показаны положения и соотношение Рамановских пиков оксида графена и температурно-восстановленного графена (ТВГ). Были сняты микрофотографии на сканирующем электронном микроскопе, а также методом ЭДС был определен элементный состав ТВГ при различных температурах. Полученные результаты по элементному анализу хорошо согласуются с данными по потери массы ТВГ, что в свою очередь объясняется удалением функциональных групп.

Ключевые слова: графен, оксид графена, температурно-восстановленный графен, Рамановская спектроскопия, энергодисперсионная рентгеновская спектроскопия, энерго-дисперсионный анализ.

Introduction

Graphene and its related structures has become the most interesting object of research in the field of science and technology, due to their unique mechanical, electrical and optical properties. One of the indicators of physical-mechanical properties (micro hardness, electrical conductivity, optical characteristics) of graphene is the elaboration of composite materials have been modified with carbon nanostructures [1, 2]. In addition, graphene and its related structures are regarded as promising materials in the production of electronic devices, electrical sources, in particular, lithium-ion batteries, can also be used in a wide variety of industries: Nano electronics, aircraft building, military equipment and medicine [3, 4]. Even having the above properties, until now, researchers have worked the problem of large-scale and more accessible technology for the production of graphene and graphene-like materials. At the present time, one of the simplest technologies for the production of graphene in large volumes is the reduction of graphene oxide [5]. Therefore, many researchers in this field have worked in obtaining graphene from graphene oxide and the study of its properties after heat treatment as a result of which the functional groups have been removed.

Graphene oxide is one sheet of the crystal lattice of graphite oxide, which is a compound of carbon, hydrogen and oxygen in various ratios, which has been formed when treatment graphite with strong oxidants [6].

Graphene oxide is synthesized from graphite by the Hammers method. Graphite is oxidized to graphene oxide with the addition of oxidants, such as potassium permanganate, sodium nitrate and concentrated sulfuric acid, followed by a three-phase procedure with low, medium and high temperature reactions [7].

The most attractive property of graphene oxide is the reduction of GO to graphene-like sheets by the removal of oxygen-containing groups. The reduced sheets of graphene oxide are usually regarded as one types of the chemically produced graphene. Reduced graphene oxide (RGO) also has a number of other names such as functionalized graphene, chemical modified graphene, chemically converted graphene or reduced graphene [8].

There are the following processes for the reduction of graphene oxide:

1. Chemical reduction with various reagents, mainly hydrazine [9];
2. Thermal reduction, which can be performed by microwave or in different atmospheres (argon, vacuum, hydrogen, hydrogen / argon) [10];
3. Electrochemical reduction [11];
4. Combination of various methods, such as chemical reduction / thermal annealing or thermal reduction/hydrogenation [10].

The process of temperature reduction of graphene oxide to 2000 °C has 6 important temperature zones: 140-180 °C, 180-600 °C, 600-800 °C, 800-1000 °C and 1000-2000 °C. At a temperature of 130 °C, due to the mild evaporation of intercalated H_2O molecules, a continuous intensive compression of graphene oxide crystals occurs. In the range of 140-180 °C, because of the rapid evaporation of intercalated H_2O molecules, graphene oxide crystals are partially exfoliated. In the range of 180-600 °C, the intermediate layers for all types of graphene and graphene oxide are contracted with removal of the basic carboxyl groups. Within 600-800 °C, the residual carboxyl and partially hydroxyl groups are removed as gases. Within the range of 800-1000 °C, residual hydroxyl and partially epoxy groups are removed. In the range of 1000-2000 °C, a decrease in the number of defects is observed [12].

Experimental

In this paper, we studied the thermal treatment of graphene oxide in a hydrogen atmosphere at the following temperatures: 150 °C, 300 °C, 500 °C, and 900 °C. As the initial object, we used graphene oxide from Goographene. The Raman spectrum of the GO is represented in Figure 1.

The graphene oxide spectrum (Fig. 1) shows two main modes: a D mode that arises due to the defects in hexagonal carbon network and G mode corresponding to the vibration of carbon-carbon bonds in a basal plane. The D peak of GO located at 1348 cm^{-1} and the G peak at 1576 cm^{-1}.

The figure 2 shows dry flakes of GO was performed by SEM. The microphotography clearly shows its layered structure.

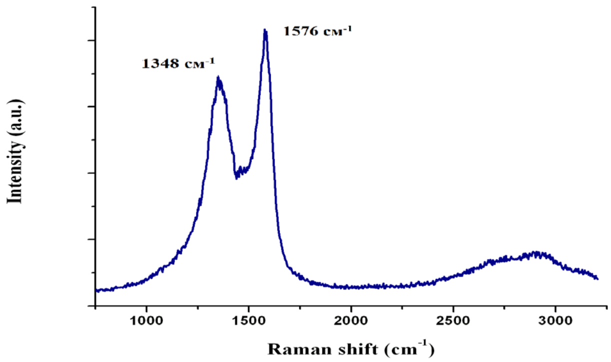
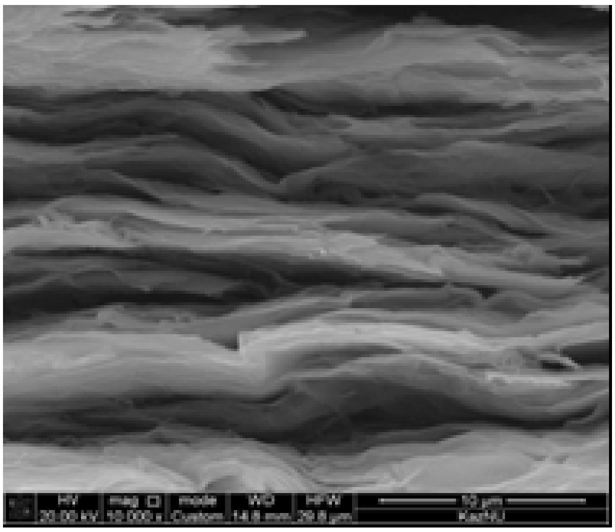


Figure 1 – Raman spectra of GO



Cross-sectional of GO
Figure 2 – SEM images of GO

Figure 3 represents the X-ray diffraction analysis of graphene oxide and HOPG was performed with the DRON-7. The interpretation of the XRD shows the interlayer spacing in the initial graphene oxide (d = 0.79 nm) and in graphite (d = 0.35 nm).

Using thermogravimetric analysis, we determined the change in mass under the effect of temperature. Thermogravimetry or thermogravimetric analysis (TGA) is a method of thermal analysis, in which the change in sample mass is recorded; changes in the physical and chemical properties of materials are measured as a function of temperature [13].

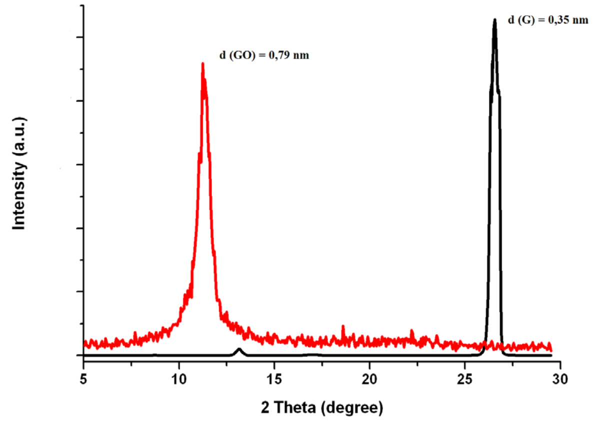


Figure 3 – X-ray diffraction (XRD) analysis of GO, HOPG

Thermogravimetric analysis of the RGO was carried out in a flow tube in a stream of hydrogen at temperatures of 150 °C; 300 °C; 500 °C; 900 °C and their masses were recorded using a Sartorius device. The masses of these samples were measured before and after annealing, then the masses of the removed chemical functional groups of the RGO were calculated.

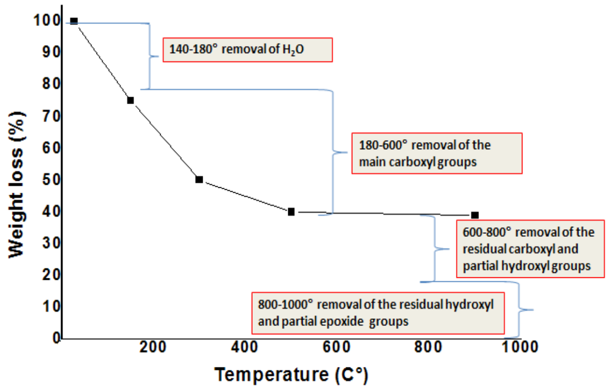


Figure 4 – TGA of RGO in a hydrogen atmosphere at different temperatures

Figure 4 shows the thermogravimetric analysis of graphene oxide reduced in a hydrogen atmosphere at different temperatures. This graph represents the loss of mass and the removal of certain functional groups of graphene oxide as the temperature rises.

In this graphical image (Fig. 4), a thermal reduction process can be observed which includes four important temperature zones in which the chemical functional groups from the RGO are removed. At temperatures 140-180 °C water is removed; 180-600 °C, the basic carboxyl groups are removed; 600-800 °C, the residual of carboxyl and partially hydroxyl groups are removed, and 800-1000 ° C, the residual of hydroxyl and partially epoxy groups are removed.

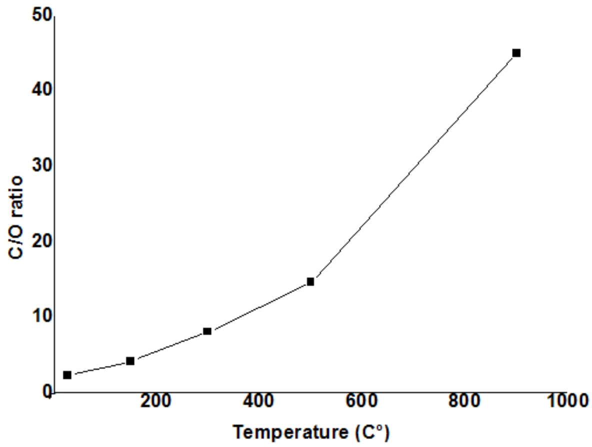


Figure 5 – Elemental analysis C/O ratio of RGO under hydrogen atmosphere

Quantum 3D 200i EDXS equipment was used to determine the elemental analysis of the RGO. The method of energy-dispersive X-ray spectroscopy is an analytical technique for elemental analysis of a solid substance, which is based on an analysis of the energy of emission of its X-ray spectrum.

Figure 5 shows an elemental analysis of GO and RGO in a hydrogen atmosphere at different temperatures. We conducted an elemental analysis of 4 samples of RGO in a hydrogen atmosphere at temperatures of 150 °C, 300 °C, 500 °C, and 900 °C. According to this graph, it is observed that as the temperature increases, the atomic fraction of oxygen decreases. Elemental analysis of each sample by temperature shows the change in the percentage of atomic weight, that is, at a temperature of 150 °C, the atomic ratio of C/O is 4.18; at 300 °C, the atomic ratio of C/O is 8.09; at 500 °C, the atomic ratio of C/O is 14.31; at 900 °C, the atomic ratio of C/O is 45.08. This elemental analysis confirms the change in the C/O ratio and the decrease in the atomic mass of oxygen with increasing temperature.

The results of thermogravimetric and elemental analysis on the isolation of functional groups and the decrease in oxygen as a function of temperature according to the known studies [14, 15, 16, and 17] depend on the strong or weak binding energy between carboxyl, hydroxyl, epoxy groups and RGO.

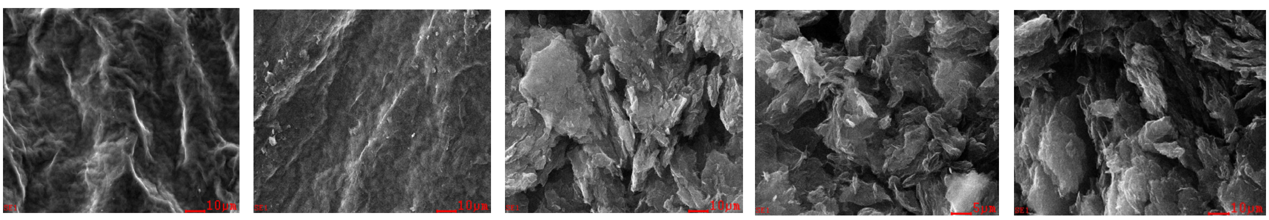
The table 1 shown the position and ratio of Raman peak of GO and RGO

Table 1 – Position and ratio of peaks in the Raman spectrum of GO and RGO at different temperatures

Samples, °C	G – band (cm^{-1})	D – band (cm^{-1})	G/D
GO	1576	1348	1,16
RGO 150 °C	1576	1348	1,07
RGO 300 °C	1579	1354	1,11
RGO 500 °C	1589	1354	1,2
RGO 900 °C	1586	1348	1,04

Figures 6 (a, b, c, d, e) show micrographs of GO and RGO at various temperatures. The micrographs were investigated by SEM. As the temperature increases and as the water and functional groups are separated out, the specific surface area of the reduced graphene oxide increases.

Based on the obtained electronic images, it can be concluded that the RGO has a developed layered structure, which in turn can be considered as promising materials in the production of electronic devices, electrical sources, in particular, lithium-ion batteries, and can also be used in gas sensors, biosensors.



a) GO b) RGO 150 °C c) RGO 300 °C d) RGO 500 °C e) RGO 900 °C

Figure 6 – Micrographs of GO and RGO

Conclusion

We investigated graphene oxide reduced in a hydrogen atmosphere at the following temperatures: 150 °C, 300 °C, 500 °C, and 900 °C. In this paper we have studied the loss of mass and the removal of the chemical functional groups of graphene oxide reduced by annealing in a flow tube in a stream of hydrogen. The result of thermogravimetric analysis in a hydrogen atmosphere showed that at a temperature of 150 °C the bulk mass leaves, from 300-900 °C the separation of functional groups is much weaker. In addition, element analysis by EDXS method was performed, which demonstrates a decrease in the oxygen level. The temperature changes in the rate of separation of functional groups and oxygen coincide with the known results and are supposedly associated with the binding energies of the groups.

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