Synthesis and analysis of nanostructured graphene oxide

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Work has been carried out to improve the method for obtaining and further oxidizing Graphene Oxide (GO) to obtain functionalized layers with a large number of active centres. We have determined that with an increase in the amount of H_2O_2 in the synthesis, it significantly increases the efficiency of the oxidation process and increases the number of functional groups, while the amount of $NaNO_3$ and $KMnO_4$ remains unchanged. Fourier-Transform Infrared Spectroscopy (FTIR), X-ray analysis, Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) analyses were carried out. Based on the FTIR result, all putative functional groups for a given material (GO) were determined, such as carbonyl, hydroxyl, ketone and epoxy groups which chemically bonded with graphene. SEM and TEM drawings were analysed, which gave a broad understanding of the morphology of GO nanostructures and, based on these drawings, it is fashionable to say that the material is semi-crystalline with the presence of such by-products as amorphous carbon nanoparticles. Based on the EDX analysis, it was proved that this nano-structured material does not have third-party products.

1. Introduction

One of the main problems of our century is the creation and design of new materials and applications in fine organic synthesis to develop the latest technologies for the production of new bioactive materials and new biocontrolled synthons [1]. When creating new composite materials, R&D teams need to be clear about the direction in which the product should be applied. Nanoparticles of carbon allotropic modifications are widely used in biomedicine, electronics, and the weapons industry [2,3]. Based on all this, we set out to synthesize graphene oxide nanoparticles, and develop a method for obtaining more functionalized ones and thereby synthesize them to determine their structure morphology. Since we live in the 21st century, most composite materials (polymers/GO nanoparticles, biodegradable polymers/GO nanoparticles) are used as additives to building materials to improve physical and mechanical properties and also for drug delivery [4,5,6]. Analyzes of the few layer grapheme oxide sample were performed witt various research methods [8-12]. After doping the grapheme – based samples with various metals, its analysis was conducted and unique result were obtained [13-15].

2. Experimental details

2.1. Synthesis and characterization of Graphene Oxide
Based on the Hammer method [2], we have created a new technique for obtaining thinner and more functionalized GO layers. Three plastic sample containers containing 2 g of graphite, 1 g of $NaNO_3$ and 6 g of $KMnO_4$ were weighed. 46 ml of 95-98% sulphuric acid (H_2SO_4) was placed in a 250 ml graduated cylinder. For testing purposes, the ice bath was filled with ice. Since two reactions were described in the planned chemistry, this approach was used twice. After sample

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preparation, three-necked and two-necked flasks were taken, as well as suitable flask thermometers. The ice bath was filled with necked flasks. Thereafter, weighed graphite, $NaNO_3$ and H_2SO_4 were added in that order. A thermometer is placed in the flask and stirring is started. We had to wait 20 minutes for the temperature to drop to 0°C. After reaching 0° C., the ice bath was removed and the temperature of the mixture began to rise. A hot plate was also used throughout this operation to reach 20°C in a shorter time.

KMnO$_4$ was gradually added over two hours when the temperature reached 20°C. We used an ice bath to keep the temperature between 20 and 25°C as the temperature increased with the addition of KMnO$_4$. After adding all of the KMnO$_4$, the mixture was stirred for another 4 hours. The temperature during these hours was regulated from 20 to 25 degrees Celsius. When the temperature rose to 35°C, the mixture was stirred for 30 minutes at this temperature. The mixture was then placed in an ice bath. The sample was gradually filled with 92 ml of DW. During this procedure, the temperature rapidly rose to 90°C and then dropped to 70°C. The temperature was maintained at 70-75 degrees Celsius for 15 minutes, and a hot plate was used to maintain this temperature. The contents of the necked flask were transferred to a 1 L Erlenmeyer flask. The necked flask was then rinsed with 280 ml DW to facilitate dispersion and reduce product loss. For this step, we prepared 500 ml of 3% H_2O_2, added it to the mixture and stirred for 10 minutes. The combinations were then allowed to stand for 12 hours. Finally, we started the filtering procedure. We used DW to wash our goods throughout the filtration process to remove sulphuric acid.

Fig. 1. Graphene oxide synthesis experiment.

2.1.1. FTIR analysis

According to FTIR results, we can say that GO has been synthesized completely. The FTIR results of GO has been compared with FTIR data base spectres from the other research papers. Result showed that the predicted functional groups could be obtained completely.

3200.1 cm^{-1}	OH group [7]
2883.6 cm^{-1}	-C-H [7]
1710.6 cm^{-1}	C=O [7]
1620.1 cm^{-1}	C=C [7]
1040.7 cm^{-1}	C-O [7]
970.06 cm^{-1}	Vinyl [7]

FTIR analysis is useful for the study of intermediate compounds formed after the oxidation process, as we oxidized our GO using H_2O_2. If you look at the result of FTIR analysis in Figure 2, you can notice that the wide peak between 3000-3750 sm^{-1} (cm^{-1}), corresponds to the stretching vibration of the groups. This fact proves to us that water molecules were adsorbed during the reaction.
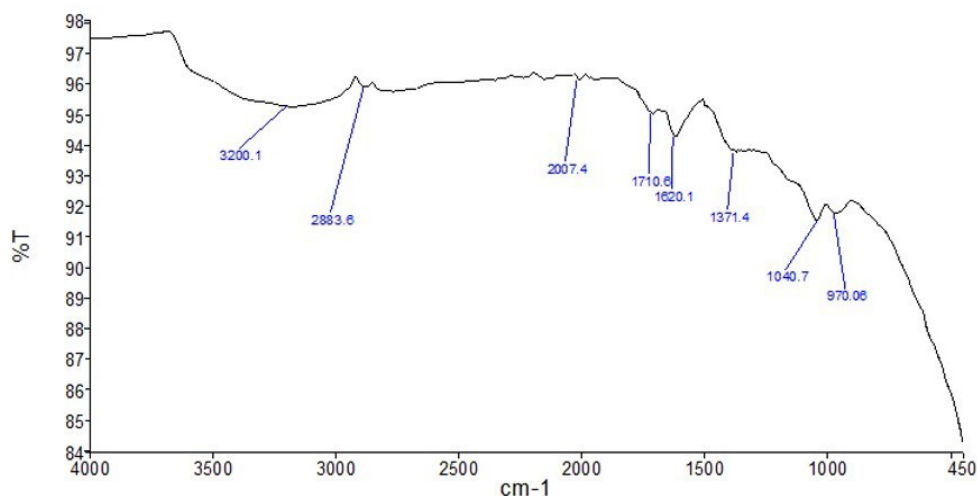

Fig. 2. FTIR result of graphene oxide

Peak 2883.6 cm^{-1} which is the absorption peak providing information for vibration of stretching C-H, while the peak of the struggle at 1710.6 cm^{-1} may be associated with the bending vibration of deformation for communication C=O. We can also say that 1620.1 (sm^{-1}) (cm^{-1}) can be associated with bending vibration of deformation for a double bond C=C, since our GO is layered material and the presence of double C=C relationships. Finally, absorption peaks at 1040.7 sm^{-1} (cm^{-1}) and 970.06 sm^{-1} (cm^{-1}) correspond to vibration of deformation related to C-O and vinyl groups. The above oxygen groups, or rather their presence, proves that this reaction was successful and the graphite was oxidized. The formation of hydrogen bonds between graphite and water molecules is observed. The formation of these bonds is provoked by surface and polar hydroxyl groups. This fact additionally explains to us the hydrophilic nature of GO.

The FTIR results of GO has been compared with other FTIR spectra in other research papers. Result showed that the predicted functional groups could be obtained completely.

2.1.2. TEM analysis

Using a 120 kV JEOL JEM-1400 transmitter electron microscope equipped with a side camera, we obtained a high-resolution image.

GO-H2O-coated carbon networks were shown at 120 kV in different magnification ranges. We used copper nets, which in turn were equipped with a carbon support film. The GO-H2O solution was applied directly to the TEM networks with a carbon support film and the network was dried overnight at room temperature. The diffraction scheme of the GO monolayer and multilayer's was recorded in diffraction mode using a microscope.

The data were collected at 10,000x magnification using a second electronic detector (SED) in 30 kV high vacuum mode.

In Figure 3 we can see that carbon and oxygen are shown in gray and black as they are heavy atoms. In Figure 4 we can see that our laminate has some holes. The more the electron beam deviates, the darker the part in this figure is indicated, and in our case, these dark parts are GO nano-sheets. This gray color tells us that our sample is very thin, or rather atomic, which indicates the correct preparation of the sample for the analysis. The black parts of this picture tell us that this

thin sheet of GO can be wrinkled somewhere and also some holes can be observed on this structure of our substance.

Carbon Nps agglomeration type	Sizes (nm)
A	428.6
B	250
C	250
D	214.3
E	142.8
F	142.8
G	250
H	214.3
I	178.6
J	214.3
K	214.3
L	200

In this table, we can observe the sizes of agglomerations of carbon nanostructures. The largest in size is agglomeration "A" with a size of 428.6 nm. Figure 6 also clearly shows amorphousness ("Bα") around agglomeration "B". Discussing these figures, we can say that our substance is semi-crystalline. We came to this conclusion because the figure has clearly marked boundaries that indicate the crystalline structure of our substance, as well as iridescent unstable boundaries that tell us about the amorphous structure of our substance.

As we can see from the Figure 3, our analysis yielded not only semi- crystalline graphene oxide nanoparticles but products like carbons and side-products like spherical carbon nanoparticles. This trend can also be seen in Figure 4 where we can observe meza-porous carbon nanoparticles. It can also be assumed that these are carbon nanoparticles are combined with amorphous carbon.
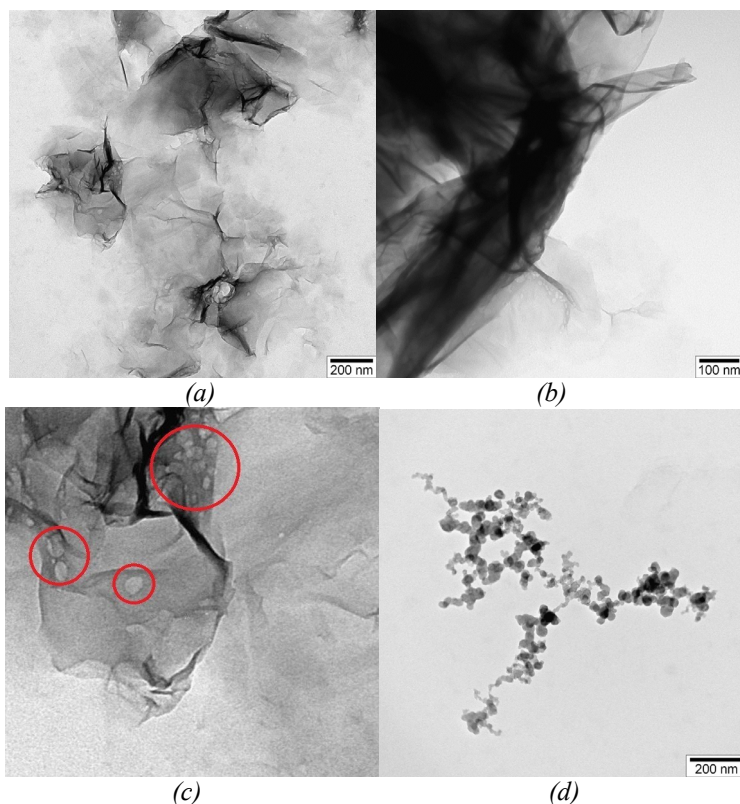

(a) *(b)*

(c) *(d)*

Fig. 3. TEM images of GO(a,b), TEM images of GO (mentioned holes) (c), TEM images of Carbon Nanoparticles (d).
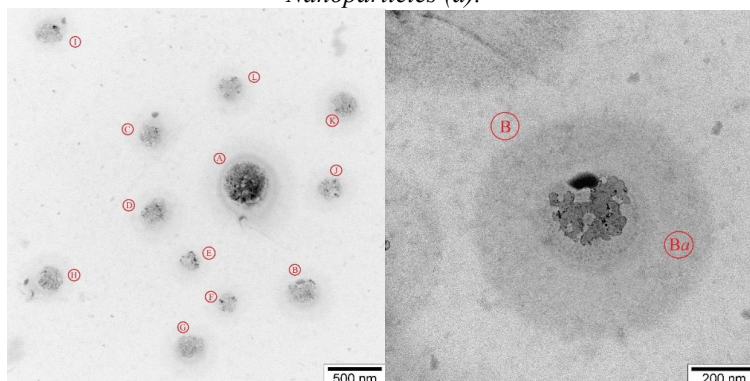

Fig. 4. TEM images of Carbon Nanoparticles Agglomerations.

2.1.3. SEM analysis

For SEM analysis, we used an apparatus called Vega 3 Tescan. Pathfinder software was used for elemental analysis.

The result of SEM analysis for graphene oxide is shown in Figure 5. The magnification of the image was taken at 3000x magnification and at the 15 kV. The distance between the optical lens and the GO sample was 5 mm. The result indicates that the typical surface morphology of the graphene oxide has well observed and shoe a porous interlinked three-dimensional graphene layer. The SEM drawing gives us such an idea about our material that GO nanoparticles is a layered material. Since we used a 1% solution of GO with water, we can see that the substrate of the SEM apparatus is very clearly seen in the figure. This fact tells us about the subtlety of our product. We can also observe some bends in this SEM image which tell us about wrinkles and some bulges. The apparently prominent white pieces may also be a clump of electrons.
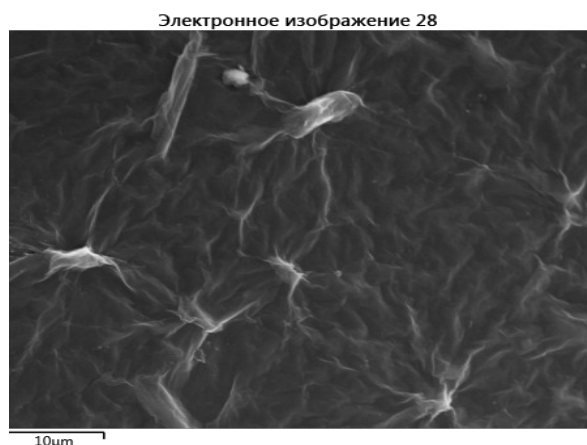

Fig. 5. SEM image of grapheme oxide.

2.1.4. EDX analysis

The data that is generated by EDX analysis (Figure 6) consists of spectra with peaks corresponding to all the different elements that are present in the sample. Every element has characteristic peaks of unique energy, all extensively documented.

For EDX analysis, we no longer used the solution, since for elemental analysis, the radiation emanating from the gun penetrates into a deeper part and we needed a thicker sample. The elemental analysis result obtained from EDS analysis shows that the majority of the content of

the compound is carbon (with 70% of mass) and following with oxygen (with 30% of mass) which proves the existence of graphene oxide. We can also observe some platinum (Pt) in our EDX analysis. This is due to the fact that, before starting elemental analysis, we pollinated our GO sample with platinum.
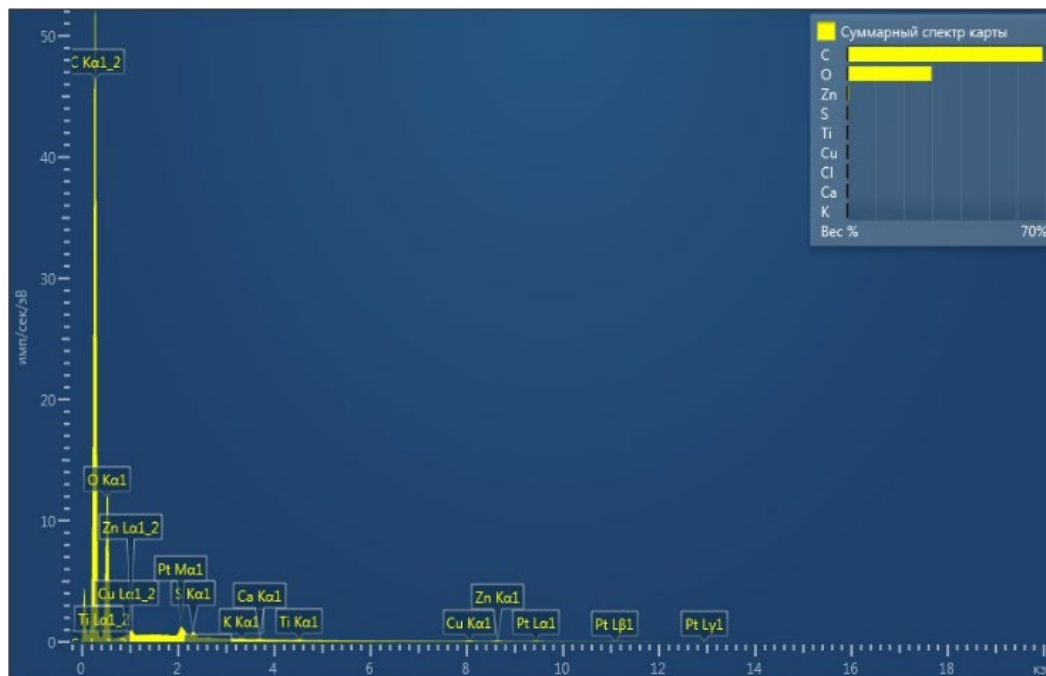

Fig. 6. EDX results of graphene oxide.

2.1.5. XRD analysis

The X-ray diffraction scattering method is considered one of the main methods for studying the structural properties of graphene oxide samples. X-ray phase analysis was carried out in the D2 Phaser diffractometer manufactured by the German "Bruker" company, with CuK_α - rays ($\lambda=1.5406$Å) in the angle interval $2\theta=0.5^0 \div 80^0$ [12]. The structural properties of graphene oxide obtained by the Hammer method were studied by X-ray phase analysis and corresponding carbon peaks were observed in the spectrum. Two visible peaks are observed in the spectrum. The spread of these peaks can be explained by the smaller particles.
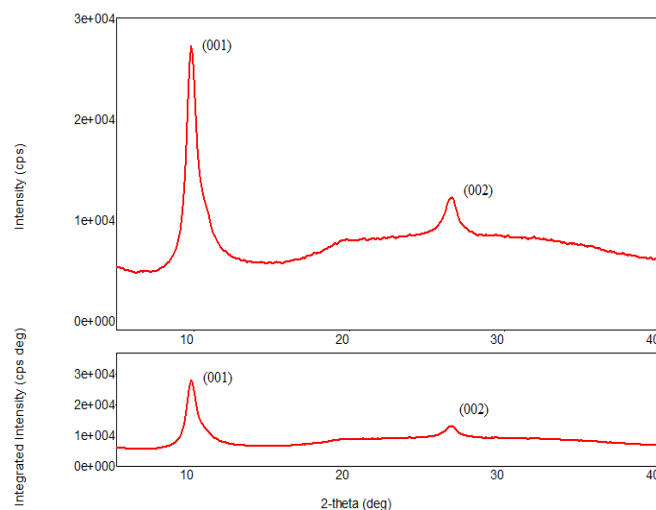

Fig. 7. X-ray diffraction of graphene oxide.

As we can see in Figure 7, the X-ray diffraction peak for GO is clearly observed at 9.8°, so the inter-layer distance will be (d) equal to 0.905 nm, this peak has been designated by index (001). Also in the figure, one more peak can be observed which is at 27°, the inter-layer ratio for this peak is 0.334 nm, this peak was designated by index (002).

3. Conclusions

Graphene oxide with the best functional characteristics has been synthesized. The obtained graphene oxide was analysed by such methods as IR, XRD, SEM and TEM. The morphology of graphene oxide layers has been studied. During the synthesis of graphene oxide in the laboratory, a new synthesis technique was applied in order to enrich graphene oxide layers with functional groups for its further functionalization. A technique for obtaining more oxidized GO has been developed. Then GO NPs have been synthesized. Finally, morphology of the resulting graphene oxide have been studied.

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