

IRSTI 31.15.35

G.K. Sugurbekova | ©



Doctor of Chemical Sciences

ORCID

<https://orcid.org/0000-0002-6894-7247>Eurasian National University named after L.N. Gumilyov,
Astana, Kazakhstansugurbekova.g.55@gmail.com<https://doi.org/10.55956/ROYK6725>

THE SYNTHESIS AND PHYSICO-CHEMICAL CHARACTERIZATION OF GRAPHENE OXIDE AND REDUCED GRAPHENE OXIDE

Abstract. In this study, we describe the synthesis and structural, morphological and physico-chemical characterization of GO and RGO. GO is obtained from graphite by using the modified Hummers method, and chemically reduced with hydrazine monohydrate to achieve reduced graphene oxide (RGO). The structure, morphology and quality of GO and RGO are described by Fourier Transform Infra-Red (FTIR) analysis, Energy dispersive X-Ray spectroscopy (EDS). The results of analysis show that GO is successfully oxidized from graphite and is effectively reduced to RGO.

Keywords: Graphene oxide, Reduced graphene oxide



Sugurbekova G. The synthesis and physico-chemical characterization of graphene oxide and reduced graphene oxide // *Mechanics and Technology / Scientific journal*. – 2023. – No.1(79). – P.191-197. <https://doi.org/10.55956/ROYK6725>

Introduction. Graphene is a single layer of carbon atoms densely packed into a crystal lattice and, due to its unique structural, mechanical and electronic properties, is a promising universal filler [1]. Graphene oxide (GO) and reduced graphene oxide (RGO) are unique derivatives of graphene [2]. They exhibit different chemical and structural properties, as they have different chemical compositions [3]. The most noticeable differences are found in the hydrophilicity, electrical conductivity, mechanical strength and dispersibility of these materials. Recently, interest in the production of materials based on graphene has increased due to its excellent properties [4].

In this study, GO powders were synthesized by the Hummers method and chemical reduction with hydrazine monohydrate [5], the resulting powders were studied by FTIR and EDS methods [6].

Conditions and methods of research. *Chemicals and apparatus.* Graphite (purity $\geq 99\%$), sulfuric acid (H_2SO_4), sodium nitrate ($NaNO_3$), potassium permanganate (purity $\geq 97\%$), hydrazine monohydrate ($NH_2-NH_2 \cdot H_2O$, purity = 98%) were purchased from Sigma-Aldrich.

Graphite, GO and RGO have been characterized using various analysis methods listed below. Fourier transform infrared (FTIR) spectra were obtained on a Thermo Scientific Nicolet iS5 spectrometer. Energy dispersive X-Ray spectroscopy (EDS) was performed in a focused ion beam scanning electron microscope (FIB-SEM) Zeiss crossbeam 540.

Preparation of GO and RGO. GO was synthesized according to the modified Hummers method [7], as described in [8]. The resulting GO is chemically reduced with hydrazine monohydrate.

Research results and discussions. Figure 1 shows the FTIR spectrum of graphite, GO and RGO and they interpretation [8]. According to the data available in the literature, absorption IR bands in the range of 3000–3500 cm^{-1} can be attributed to stretching vibrations of O-H bonds. The IR absorption band located at around 870 cm^{-1} is characteristic of off-plane vibrations of the C-H group in the aromatic ring [9]. The IR absorption band 1644 cm^{-1} can be assigned to the C=C bonds (Table 1). FTIR used to investigate the bonding interactions in the samples. The result indicates that consist of carbonyl C=O, aromatic C=C, carboxyl CO, epoxy C-O-C, alcoxy and hydroxyl O-H, whereby wide peak at 3091 cm^{-1} are corresponding to the O-H (hydroxyl) groups and can be [10]. This region of the spectrum can overlap with vibrations of CH and CH₂ groups of the GO skeleton and represent the hydroxyl group in GO network, which reduce the intensity after oxidation of graphite [9].

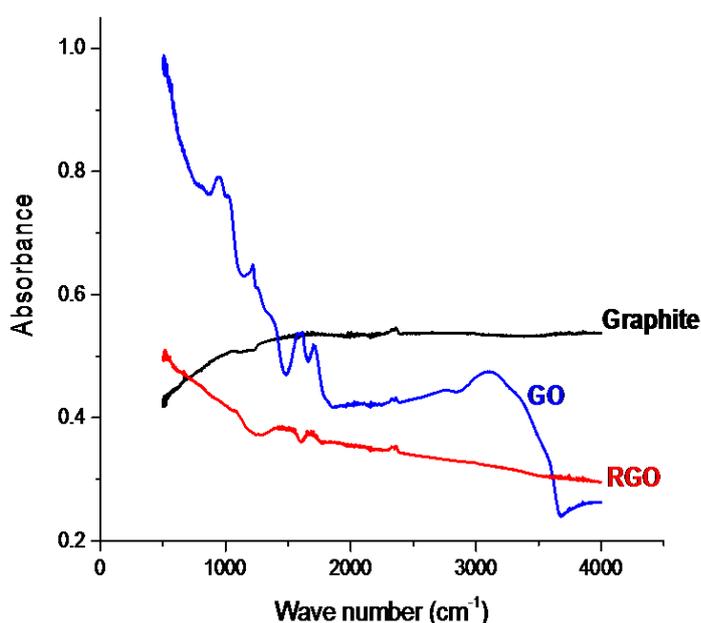


Figure 1. FTIR spectrum of graphite, GO and RGO

The wide and complex band near 3091 cm^{-1} in FTIR spectra of GO represent as –OH stretching vibration and symmetric and asymmetric stretching vibration of –CH₂ – [11], as those reported in work [12].

Groups of bands are observed in the IR spectrum of graphene materials. Intense bands in the region of 1700–1450 cm^{-1} , which correspond to stretching vibrations of the carbon plane of graphene. In the region of 1450–1000 cm^{-1} , the most intense vibrations correspond to deformation vibrations of the graphene plane and deformation vibrations of terminal C – H bonds. The intense band (about 942 cm^{-1}) corresponds to off-plane vibrations of the CH bonds. While peak at ~2358 cm^{-1} (graphite) and 2368 cm^{-1} (GO) is corresponded to the peak for carboxylic group -COOH [9].

Table 1

Assignment of the IR absorption bands of GO Assignment of characteristic IR absorption bands of graphite, GO and RO

Sample	Frequency, (cm ⁻¹)	Communication / Functional Group	References
Graphite	3091 wide band	Valence O-H bond vibrations	[9]
	1644	C=C benzene ring	[10]
	1140	Valence vibrations of C-O bonds	[9]
	1032	C-O-C bonds	[10]
	871	C-H bonds of the aromatic ring	[9]
	2358	Carboxylic acid group - COOH	[11]
	1684	C=C stretching aromatic benzene ring	[11]
	1558	skeletal vibrations of graphitic domains	[10]
GO	3091 wide band	-OH stretching vibration, symmetric and asymmetric stretching vibration of -CH ₂ -	[9]
	1700	C=O stretching vibration carboxylic acid and carbonyl groups	[10]
	1616	Deformation vibration of OH group	[12]
	1219	C-O-C stretching of epoxy group	[11, 12]
	1080	C-O stretching of alkoxy group	[9]
	942	C-H bonds of the aromatic ring	[10]
RGO	2368	Carboxylic acid group-COOH	[11]
	1652	C=C stretching aromatic benzene ring, skeletal vibrations of graphitic domains	[8]
	1456	Bending stretching and vibrations of the carbon plane of graphene. C=C bond (aromatic group)	[9]

On the other hand, broad peak 1456 cm⁻¹ in spectrum of RGO are corresponded to C=C bond (aromatic group) [12]. T. Sakthivel et al declared as C-O (carbonyl and carboxyl) group at band ~1558 cm⁻¹ [13]. The band between 1080 cm⁻¹ in FTIR of GO is corresponded to C-O-C (epoxy) groups [12]. It can assume graphite powder successfully oxidizing. The oxidation of graphite is accompanied by significant

changes, as the FTIR spectra of graphite and GO show perfectly. Also, changes in the structure of RGO are accompanied by the recovery process of GO. In the FTIR spectrum of RGO there are no characteristic frequencies of some oxygen-containing groups. The oxidation of graphite is accompanied by a change in structure. In addition to the appearance of new groups, the nature of the bonds of the carbon plane also changes. With the addition of oxygen atoms, the hybridization of carbon atoms of the graphene plane changes from sp^2 to sp^3 . The addition of various oxygen-containing groups leads to a change in bond lengths and, accordingly, in the frequencies and intensities of vibrations.

The FTIR spectrum of GO shown in Figure 2 confirms the introduction of oxygen containing groups such as functional hydroxyl, epoxy and carboxylic groups upon oxidation of sugarcane bagasse. The strong band at 1700 cm^{-1} is attributed to stretching vibration modes of C=O in carboxylic acid and carbonyl groups. The peak at 1558 cm^{-1} is assigned to the skeletal vibrations of un-oxidized graphitic domains. The band at 1080 cm^{-1} is assigned to C–O (epoxy) groups while the band at 1219 cm^{-1} is usually attributed to C–OH stretching vibrations. The strong peak around $3000\text{--}3600\text{ cm}^{-1}$ can be attributed to the O–H stretching vibrations of the C–OH groups and water. Thus the result obtained from FTIR affirmed the presence of various oxygen containing functional groups like hydroxyl, epoxy, carboxyl, carbonyl within the GO structure.

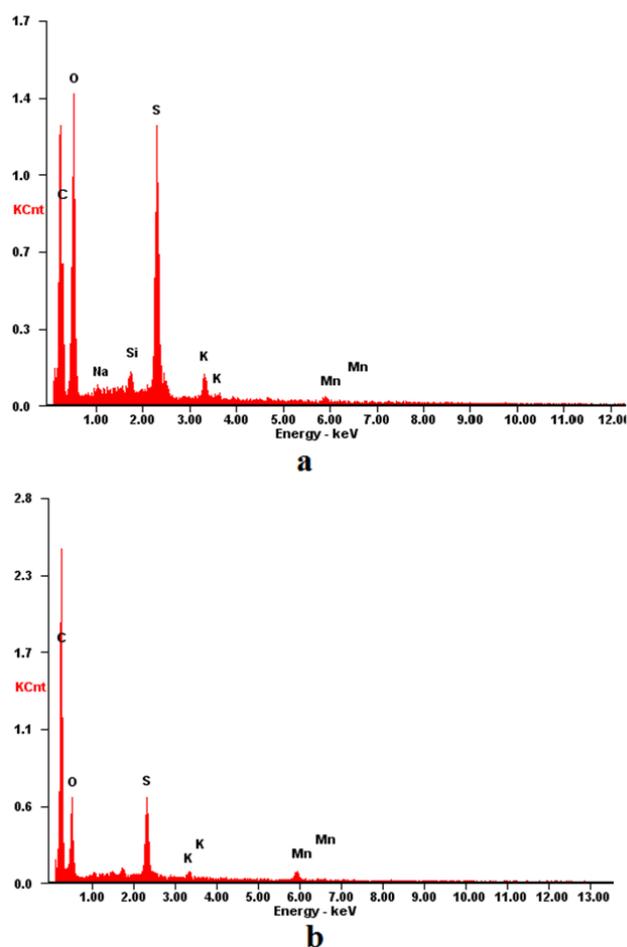


Figure 2. EDS spectra of (a) GO and (b) RGO

The EDS spectrum of GO reveals the content of carbon, oxygen, sodium, silicon, sulfur, potassium and magnesium. Sulfur and potassium are coming from H_2SO_4 and $KMnO_4$ used as oxidizing agent, while sodium, silicon and magnesium are from the substrate. These data confirm that GO is formed [14]. The EDS spectrum of RGO also highlights the content of carbon, oxygen, sodium and magnesium. In addition, a reduction in percentage of sulfur and potassium is observed when compared to EDS spectrum of GO. Table 2 gathers the elemental composition of both GO and RGO [15]. It can be noticed that during the reduction of GO with hydrazine monohydrate, sodium and silicon are completely reduced. The carbon content in the RGO increases from 52.06% to 71.61%, whereas oxygen content decreases from 31.41 to 17.22% [16]. This result shows that hydrazine monohydrate reduced GO to RGO to a certain extent.

Table 2

Elemental composition of GO and RGO

Elements	GO		RGO	
	Mass fraction (%)	Atomic fraction (%)	Mass fraction (%)	Atomic fraction (%)
Carbon	52.06	63.80	71.61	81.37
Oxygen	31.41	28.89	17.22	14.69
Sodium	0.31	0.20	-	-
Silicon	0.78	0.41	-	-
Sulfur	12.31	5.65	6.16	2.62
Potassium	1.94	0.73	0.70	0.25
Magnesium	1.18	0.32	4.32	1.07
Total	99.99	100	99.99	100

Conclusion. In this work, GO and RGO were successfully obtained. GO was obtained using the modified Hummer method with monohydrate hydrazine and reduced to RGO. According to the GO FTIR spectrum, it can be concluded that they contain oxygen functional groups, due to the oxidation of graphite and the formation of GO. According to the EDS spectrum of the RGO the oxygen content decreased and the carbon content increased in comparison with GO.

References

1. Allen M.J., Tung V.C., Kaner R.B. Honeycomb carbon: A review of graphene // *Chemical Reviews*, 2010. Vol. 110, No. 1, P. 132-145. <https://doi.org/10.1021/cr900070d>.
2. Novoselov K., Fal V., Colombo L., Gellert P. (2012) A roadmap for graphene // *Nature*, 2012. Vol. 490, No.7419, P. 192–200. <https://doi.org/10.1038/nature11458>.
3. Bao Q., Eda G., Chhowalla M. Graphene oxide as a chemically tunable platform for optical applications // *Nature Chemistry*, 2010. Vol. 2, No 12, P. 1015-1024. <https://doi.org/10.1038/nchem.907>.
4. Kudaibergenova R.M., Nurlybayeva A., Kantarbayeva S.M., Matniyazova G.K., Baibazarova E., Sugurbekova G.K. Unique properties of graphene // *News of the Academy of sciences of the Republic of Kazakhstan*, 2020. Vol. 4, No. 442, P. 80-88. <https://doi.org/10.32014/2020.2518-1491.68>

5. Park S., Ruoff R.S. Chemical methods for the production of graphenes // *Nature Nanotechnology*, 2009. Vol. 5, No. 4, P. 217-224. <https://doi.org/10.1038/nnano.2009.58>.
6. Pei S. The Reduction of graphene oxide, *Carbon*, 2012. Vol. 50, No. 9. P. 3210–3228. <https://doi.org/10.1016/j.carbon.2011.11.010>
7. Offeman R., Hummers W. Preparation of graphitic oxide // *Journal of the American Chemical Society*, 1958, Vol. 80, No. 6, P. 1339-1339. <http://dx.doi.org/10.1021/ja01539a017>
8. Kudaibergenova R., Ualibek O., Sugurbekov E., Demeuova G., Frochot C., Acherar S., Sugurbekova G. Reduced graphene oxide based superhydrophobic magnetic nanomaterial as high selective and recyclable sorbent for oil/organic solvent wastewater treatment // *International Journal of Environmental Science and Technology*, 2022. Vol. 19, No. 8491-8506. <https://doi.org/10.1007/s13762-021-03722-3>.
9. Hidayah N.M., Wei-Wen L., Chin-Wei L., Noriman N.Z., Cheng S.K., Hashim U. and Cheun H.L. Comparison on graphite, graphene oxide and reduced graphene oxide: synthesis and characterization // *AIP Conference Proceedings*, 2017. Vol. 1892, No. 1. P.150002. <https://doi.org/10.1063/1.5005764>
10. Manoratne C.H., Rosa S.R.D. and Kottegoda I.R.M. (2017) XRD-HTA, UV visible, FTIR and SEM interpretation of reduced graphene oxide synthesized from high purity vein graphite // *Material Science Research India*, 2017. Vol. 14, No. 1. P. 19-30. <https://doi.org/10.13005/msri/140104>
11. Tarko F.E., Delele W.A. Controlled synthesis, characterization and reduction of graphene oxide: a convenient method for large scale production // *Egyptian Journal of Basic and Applied Sciences*, 2017. Vol. 4, No.1. P. 74-79. <https://doi.org/10.1016/j.ejbas.2016.11.002>
12. Zhu Y., Murali S., Cai W., Li X., Suk J.W., Potts J.R. and Ruoff R.S. Graphene and graphene oxide: synthesis, properties, and applications // *Advanced Materials*, 2010. Vol. 22, P. 3906-3924. <https://doi.org/10.1002/adma.201001068>
13. Sakthivel T., Gunasekaran V., and Kim S. J. Effect of oxygenated functional groups on the photoluminescence properties of graphene-oxide nanosheets // *Materials Science in Semiconductor Processing*, 2014. Vol. 19, No. 1. P. 174-178. <https://doi.org/10.1016/j.mssp.2013.12.015>
14. Cunha E., Ren H., Lin F., Kinloch I.A., Sun Q., Fan Z. The chemical functionalization of graphene nanoplatelets through solvent-free reaction // *Royal Society of Chemistry Advances*, 2018. Vol. 8, P. 33564-33572. <https://doi.org/10.5772/intechopen.84527>
15. Zhang H. and Feng P.X. Fabrication and characterization of few-layer graphene // *Carbon*, 2010. Vol. 48, No. 2. P. 359–364. <https://zh.booksc.eu/book/3457319/059f12>
16. Soldano C., Mahmood A., Dujardin E. Production, properties and potential of graphene // *Carbon*, 2010. Vol. 48, No. 8. P. 2127-2150. <https://doi.org/10.1016/j.carbon.2010.01.058>

Material received on 13.03.23.

Г.К. Сугурбекова

Л.Н. Гумилев атындағы Еуразия ұлттық университеті, Астана, Қазақстан

**ГРАФЕН ОКСИДІ МЕН ТОТЫҚСЫЗДАНҒАН ГРАФЕН ОКСИДІНІҢ СИНТЕЗІ
ЖӘНЕ ОЛАРДЫҢ ФИЗИКАЛЫҚ-ХИМИЯЛЫҚ СИПАТТАМАСЫ**

Аңдатпа. Бұл зерттеуде графен оксиді (ГО) және тотықсызданған графен оксиді (ТГО) синтезі мен құрылымдық, морфологиялық және физикалық-химиялық сипаттамасы берілген. ГО модификацияланған Хаммерс әдісін қолдану арқылы графиттен дайындалды және ТГО алу үшін гидразин моногидратымен химиялық тотықсызданды. ГО және ТГО құрылымы, морфологиясы және сапасы Фурье түрлендіру инфрақызыл, энергетикалық дисперсиялық рентгендік спектроскопия арқылы сипатталған. Талдау нәтижелері ГО графиттен сәтті тотықтырылғанын және ТГО-ға дейін тиімді тотықсызданғанын көрсетеді.

Тірек сөздер: графен оксиді, тотықсызданған графен оксиді.

Г.К. Сугурбекова

Евразийский национальный университет имени Л.Н. Гумилева, Астана, Казахстан

**СИНТЕЗ И ФИЗИКО-ХИМИЧЕСКАЯ ХАРАКТЕРИСТИКА ОКСИДА ГРАФЕНА И
ВОСТАНОВЛЕННОГО ОКСИДА ГРАФЕНА**

Аннотация. В исследовании описывается синтез и структурная, морфологическая и физико-химическая характеристика оксида графена (ГО) и восстановленного оксида графена (ВГО). ГО получают из графита с использованием модифицированного метода Хаммерса и химически восстанавливают моногидратом гидразина для получения (ВГО). Структура, морфология и качество ГО и ВГО описываются с помощью инфракрасного анализа с преобразованием Фурье, энергодисперсионной рентгеновской спектроскопии. Результаты анализа показывают, что ГО успешно окисляется из графита и эффективно восстанавливается до ВГО.

Ключевые слова: оксид графена, восстановленный оксид графена.