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ФУНКЦИОНАЛИЗАЦИЯ ОКСИДА ГРАФЕНА АЗОТОМ
FUNCTIONALIZATION OF GRAPHENE OXIDE BY NITROGEN**

Аңдатпа. Бұл жұмыста біз графен оксидін азотпен функционалдандырудың қарапайым әдісін қолдандық. Азотпен функционалдану әдісі графен оксидін ғылым мен техниканың әртүрлі салаларында қолдану мүмкіндіктерін едәуір кеңейтуге мүмкіндік береді. Графен оксидінің бастапқы үлгісі және жану разрядында өңдеуге арналған графен оксидінің үлгісі қабаттың қалыңдығы 10 нм-ден асатын Si/SiO₂ бетіне жағылды. Зерттеу барысында рентгендік фотоэлектрондық спектроскопия (РФЭС), Раман спектроскопиясы, сондай-ақ сканерлеуші электронды микроскопия көмегімен өңдеуге дейінгі және кейінгі графен оксиді үлгілерінің бетінің құрылымы мен химиясы сипатталды. Азоттың жану разряды арқылы жұмыс істеуі азоттың көбеюіне және оттегі деңгейінің төмендеуіне әкелді.

Түйін сөздер: графен оксиді, функционалдау, азот, жарқырау разряды.

Аннотация. В данной работе был использован простой способ функционализации оксида графена азотом. Функционализация азотом позволяет существенно расширить возможности использования оксида графена в различных областях науки и техники. Исходный образец оксида графена, и образец оксида графена для обработки в тлеющем разряде, были нанесены на поверхность Si/SiO₂ с толщиной слоя более 10 нм. В ходе исследования структура и химия поверхности образцов оксида графена до и после обработки были охарактеризованы с помощью рентгеновской фотоэлектронной спектроскопии (РФЭС), спектроскопии комбинационного рассеяния, а также с помощью сканирующей электронной микроскопии. Функционализация азотом посредством тлеющего разряда привела к увеличению азота и к уменьшению уровня кислорода.

Ключевые слова: оксид графена, функционализация, азот, тлеющий разряд.

Abstract. In this paper, we used a straightforward method for the functionalization of graphene oxide with nitrogen. Functionalization with nitrogen makes it possible to significantly expand the possibilities of using graphene oxide in various fields of science and technology. The original graphene oxide sample and the glow discharge graphene oxide sample were deposited on the Si/SiO₂ surface with a layer thickness of more than 10 nm. During the study, the structure and surface chemistry of graphene oxide samples before and after treatment were characterized using X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and scanning electron microscopy. Functionalization with nitrogen via glow discharge resulted in an increase in nitrogen and a decrease in oxygen levels.

Keywords: graphene oxide, functionalization, nitrogen, glow discharge.

Introduction. One of the most quintessential factors in nature particularly is carbon, which is quite significant. All organisms on our planet contain of carbon-based structures, and a substantially things which we eat in our each day existence are made of carbon compounds. Many allotropic compounds have been assigned to carbon. Graphite can generally be described as the allotropes shape of elemental carbon in additament to diamond. It is known that graphite has a layered covalent structure, every carbon atom frequently is bonded to three other carbon atoms. There are several important possessions of graphite: grayish black in colour, opaque substance, lighter than diamond, convenient and slippery to contact, a real conductor of electricity and warmth, a crystalline solid, non-inflammable, soft due to weak Vander wall forces. Though, diamond is known because of the hardest substance. It essentially contains a crystalline nature; every atom truly is associated with four carbon atoms. It's an inflexible bond that is tough to ruin, colorless and transparent.

Currently, carbon-based substances in current science have a top-notch attention. It is now well established from a variety of studies that it can exist in various configurations with unique properties such as fullerenes, carbon nanotubes, graphene, and its derivatives (graphene oxide), nanodiamonds as well as carbon-based quantum dots. The names of great explorers such as Robert F. Curl Jr., Sir Harold W. Kroto and Richard E. Smalley, A. Geim and K. Novoselov as well as S. Iijima will forever remain in the history of discoverers of carbon forms. Undoubtedly, such a huge interest of carbon-based materials is revealed due to ease of processability, high - temperature stability, eco - friendly and widely applied in various potential applications: gas sensing, energy storage, water treatment, biomedical, space.

Fullerenes (C_{60}) were discovered in 1985, while the discovery of the carbon nanotube in 1991 boosted the research in the field of carbon related nanomaterials. To our understanding, fullerenes square measure an element of carbon having hollow molecules, during which sp^2 -carbons square measure exactly secure to a few neighbors in an exceedingly system of five- and 6-membered rings. Fullerenes (originally Buckminster fullerenes) area unit a brand-new category of carbon-only molecules wherever sixty carbon atoms (C_{60}) area unit organized in an exceedingly ball structure. The C_{60} molecule is implausibly stable, having the ability to resist high temperatures and pressures. The exposed surface of the structure is ready to react with totally different species whereas conserving the geometry. Some studies discovered that C_{60} may be thought about as a motivating scaffold for drug delivery since it may be multi-functionalized, forms NP, and/or acts as a drug absorbent.

Moreover, the carbon nanotubes are viewed to be the cylindrical model of fullerene. Because of the very fact that carbon nanotubes are derived from fullerenes, they are guided to as tubular fullerenes or bucky tubes. The incredibly true discovery of carbon nanotubes opened a new understanding in nanotechnology, electronics, optics, and different fields of materials science. As a give up result of which carbon nanotubes describe a greater and extra essential crew of nanomaterials with incredible geometric, electronic, and mechanical yet as chemical properties. For example, according to the literature, the tensile strength of carbon nanotubes is 20 times higher than that of high-strength alloy steel, and the density is half that of aluminum. Depending upon the extent of carbon layers, carbon nanotubes are frequently labeled as single-walled carbon nanotubes, double-walled carbon nanotubes, and multi-walled carbon nanotubes. Carbon nanotubes region unit is completely utilized in drug delivery, sensing, and water treatment.

Among the families of carbon materials, graphene is still in its teenage years, in the last 18 years have passed since its discovery, and therefore remains a promising material of the future. It was surprising that isolated from graphite using a simple technique with an adhesive tape revealed the graphene. Remarkably, carbon nanotubes and buckyballs are composed of one or a few layers of graphene in a regular arrangement. In fact, that graphene is the mother of all graphitic forms

of carbon. It has been reported that graphene is a carbon material having a two-dimensional hexagonal structure in one layer, where carbon atoms are connected by sp^2 bonds that resemble honeycomb structure. Data from several studies suggest that graphene as well as graphene-like materials, also graphene oxide and other carbon materials are of great interest for the scientific community due to such peculiar properties as: high level of thermal and electrical conductivity, strength, and excellent adsorption characteristics. Extensive research has shown that graphene is attractive in many fields due to its versatility. In fact, various groundbreaking studies have revealed the following key benefits of graphene: the finest and hardest material known; flexible and transparent color; excellent thermal and electrical conductor; used in the manufacture of high-speed electronic devices; explosives detection by chemical sensors; membranes for more efficient separation of gases, made from foil with nanoscale pores; for the production of transistors operating at high frequencies; expanded production of low-cost mobile phone screens to replace indium-based electrodes in organic light-emitting devices (OLEDs); creating lithium-ion batteries that use graphene on the anode surface to recharge those batteries faster; recovery of hydrogen for fuel cell vehicles; cheaper water desalination technology that uses graphene films with nanoscale holes to separate water from ions in salt water [1].

Graphene derivatives such as graphene oxide are identified to be broadly used due to their comparable features to graphene. Graphene is viewed as the first-rate conductor of electricity due to the fact the π -electrons of the carbon atoms move freely within the crystal planes, making graphene a fantastic electrical conductor. However, graphene oxide is an insulator due to the disruption of the sp^2 -bonded community through the way of oxygen-containing groups. These functional groups make the graphene oxide surface easily modifiable with fast electron transfer kinetics and excellent hydrophilicity and biocompatibility. Modification of graphene by introducing diverse functional groups into its configuration causes it achievable to improve the properties of graphene and constantly expand the range of its application [2]. Even though graphene has outstanding properties, this is functionalized or doped to enhance or tune its properties [3]. It is worth noting that there are many ways to functionalize graphene, but one effective way is to modify graphene by substitutional doping.

Various thermal, chemical, optical, and other approaches are used to functionalize and reduce graphene oxide. With the development of nanotechnology, plasma processes have been used for the growth and functionalization of nanomaterials offering a unique combination of economical and environmentally safe properties in the manufacturing process. Functionalization of graphene oxide is mainly done by plasma treatment of nitrogen, ammonia, oxygen, methane, hydrogen, and fluorine. Plasma is mainly used as rapid method to functionalize carbon nanomaterials. Compared with other methods, this plasma functionalization is an environmentally friendly technique for the surface functionalization of carbon nanomaterials. Some scientific reports presented different ways of discharges such as argon glow discharge, low-pressure radio frequency (RF) plasma activation [4] which used to functionalized nanostructures.

Graphene, which has a zero-band gap, must be functionalized with heteroatoms to open its band gap. Band gap tunable via substitution doping. Heteroatoms are used to tune and improve the band structure and conductivity [5]. The choice fell on nitrogen not by chance since its atomic size and radius are similar to carbon. Many studies have been conducted with nitrogen (N)-doping. Heteroatom dopants can be electron donors (n-type) or electron acceptors (p-type). Both B and N, the neighboring elements of C on the periodic table, easily substitute C in the graphene lattice, resulting in p- and n-type doping, respectively. According to the article, N atom is more appropriate than B atom because it is more easily substituted into graphene.

The purpose of this work was to investigate the effect of glow discharge plasma on structure as well as properties of graphene oxide.

Materials and methods of research. The synthesis of graphene oxide was done according to the procedure of Hummers [6]. A volume of 500 ml in a flask was mixed with 1 g of graphite powder and 1 g of sodium nitrate with 50 ml of concentrated sulfuric acid, which was in an ice bath, where the solution was stirred continuously for 30 minutes. Then, 6 g of potassium permanganate was carefully added to the resulting mixture to prevent an explosion, and the overheating temperature was maintained at 5°C. The resulting solution was mixed at a temperature of 35°C for 3 hours. After that, 200 ml of 3% hydrogen peroxide was added and stirred for 30 minutes. The resulting graphene oxide was washed with distilled water until pH 6 was reached. As a result, the product was dried in an oven at a temperature of 80°C for 24 h.

According to the electronic configuration, graphene oxide (GO) possesses several remarkable optical properties. It displays structure-dependent absorption and Raman spectra that depict its chemical composition and the degree of functionalization-induced disorder [7,8]. GO holds high electrical resistivity as well as high hydrophilic behavior, which permits good adherence to other materials and the possibility of preparing complicated compound structures. Electronic residences such as conductivity of GO sheets rely strongly on their chemical and atomic structures. Structure of GO has been studied with the beneficial resource of massive fluctuate of strategies.

Raman spectroscopy. This method affords facts on structural or chemical defects produced in its structure. Besides, the shape of bands, depth and width, and the characteristic of graphene oxide Raman spectrum rely on the atomic configuration. We also studied the Raman spectra of graphene oxide exposed to nitrogen glow discharge plasma. Raman spectra were obtained with a Raman spectrometer. We use Raman spectroscopy to explore the structural and electronic properties of graphene oxide.

XPS. Graphene oxide can in addition mostly be analyzed via X-ray photoelectron spectroscopy (XPS) to determine the composition of the specimen surface and accelerated curiously to figure out the ratio of individual functional groups. X-ray photoelectron spectrum of GO samples was recorded in a model ThermoFisher Scientific Nexsa X-Ray Photoelectron Spectrometer (XPS). The excitation source was the Al K α ($h\nu = 1486,68$ eV, 400 μm spot size) radiation. The equipment uses a hemispherical electron analyzer. XPS spectra were recorded at 0.1 eV analyzer pass energy. The residual pressure in the analysis chamber remains under a value of 4×10^{-7} Pa.

SEM. Scanning electron microscopy (SEM) was used to study the morphology of GO. The obtained GO samples were investigated on a SEM Quanta 200i 3D instrument. From Figure 1 b, the wrinkled structure morphology of the GO can be seen by SEM where parameters of SEM are HV=5.00 kV, magnitude= 12 000x, WD=15.1 mm, HFW=24.9 μm .

Results and discussions. Figure 1 a present a typical Raman spectrum of initial GO. In the spectral region between 1000-3750 cm^{-1} , the measurements were achieved below excitation with a 473 nm laser. The Raman spectrum of GO elicited information on G and D peaks. The G peak is reflected at about 1587 cm^{-1} , while the D peak appear in 1350 cm^{-1} . The D/G ratio, calculated from the intensity of peaks, shows the level of oxidation of the sample and in our study the D/G ratio of GO was 0.95.

XPS is used to obtain insights into changes in the surface chemical composition of GO specimens treated with nitrogen glow discharge plasma compared to pristine GO sample. Treatment significantly reduces oxygen content. In the case of XPS analysis, for all the samples analyzed, scans were recorded for C1s, O1s and N1s with a step size of 0.1 eV and pass energy of 50 eV. Figure 2 and Figure 3 show the deconvoluted C1s of the pristine and treated GO samples, respectively. The curve deconvolution of the C1s peak of the GO, which without treatment shows in Figure 2 a four peaks designated as C1 (C-C, 284.8 eV), C2 (C-O, 286.8 eV), C3 (O-C=O, 288.5 eV), C4 (C=C, 283.4 eV) [9]. For the deconvoluted C1s peak of the GO sample, which after nitrogen glow discharge plasma shown in Figure 3, where five peaks designated as C1 (C-C,

284.8 eV), C2 (C-N, 286.7 eV) [10], C3(C=O, 287.9 eV), C4 (O-C=O, 290.3 eV), C5 (C(O)OH, 283.7 eV) [11]. Plasma surface treatment leads to disappear the double bond carbon (C=C) and creates carboxylic acid (C(O)OH), carboxyl (O-C=O) as well as the appearance of an additional (C-N) bond peak.

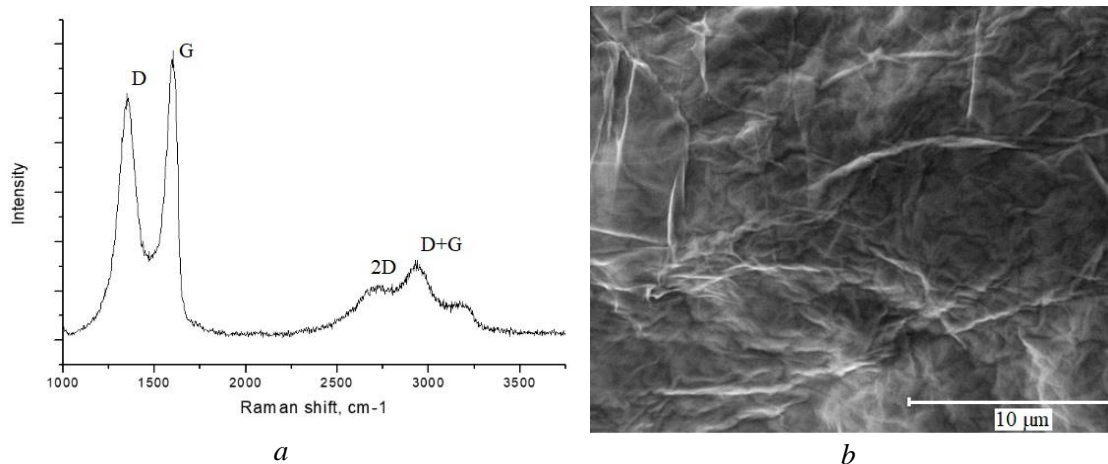


Figure 1. a – Raman spectrum of graphene oxide, with characteristic peaks, b – SEM image of GO surface

Deconvoluted O1s spectra of GO without treatment and GO after treatment are given in Figure 4 and Figure 5, respectively. The O1s spectrum of GO initial sample can be divided into O1 (532.4 eV) [12], O2 (530.8 eV), O3 (534.5 eV) [13], which is assigned to C=O, C–O, and adsorbed H₂O, respectively (Figure 4). While the O1s spectrum of the second sample (Figure 5) can be divided into O1 (C–O, 532.3 eV), O2 (O=C–O, 534.9 eV) [14], O3 (C–OH, 531.3eV) [15]. The observed functional groups such as C=O, O=C–O, and C–OH are highly affected after plasma treatment. The O1 peak is attributed to carbonyls groups. The O2 peak is associated with carboxyl, while the O3 peak corresponds to hydroxyl groups.

The N1s peak of GO sample without treatment is negligible, however, it is clearly detectable after exposure to the nitrogen plasma thus indicating that this treatment leads to functionalization of the graphene oxide with N-sites. In Figure 6, the N1s spectrum can be decomposed into four component peaks, corresponding to the bonding configurations of N1 (pyrrolic-N, 399.7 eV), N2 (the oxidized pyridinic-N (Nox), 402.7 eV), N3 (substitutional/graphitic- N, 400.6 eV), N4 (pyrrolic-N, 399.1 eV). The survey XPS spectrum of graphene oxide before treatment and after treatment through Avantage software revealed that the successful introduction of a high nitrogen content into the graphene oxide structure, where the elemental content of nitrogen in the second specimen was 9.95 at.%. By contrast, the elemental content of nitrogen in an initial graphene oxide was 0.85 at.%. (Table 1).

Table 1. Elemental composition of the obtained N-doped graphene from the XPS spectra

Sample	Element, %		
	C	O	N
GO without treatment	71.9	27.1	1.0
GO after treatment	69.6	20.5	9.9

Modification process: Functionalization was carried out on a universal vacuum unit VUP 5M.

The system was pumped down to the level of 10^{-4} Pa. The nitrogen gas was admitted to a pressure level in the chamber of the order of 10 Pa. Irradiation was carried out in a standard glow discharge system. With this in reason, current plasma experiment is worked at 1.5×10^{16} Ions/cm² dose, and acceleration voltage 2.5 kV.

The capacious work of the scientist Haifeng Xu and co-workers presented methods for the synthesis of N-doped graphene [16]. An overview of the literature confirmed that there are not enough articles in this theme [17-20].

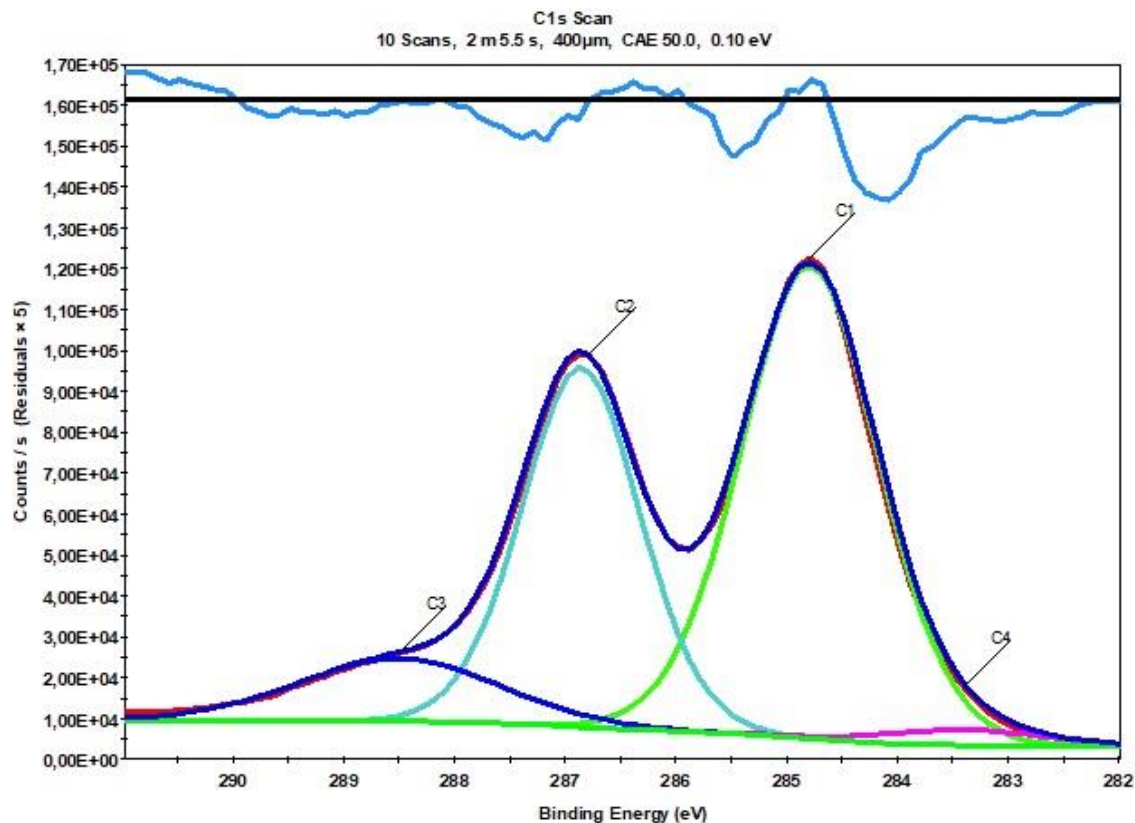


Figure 2. The C1s peaks in the XPS spectra of GO without treatment

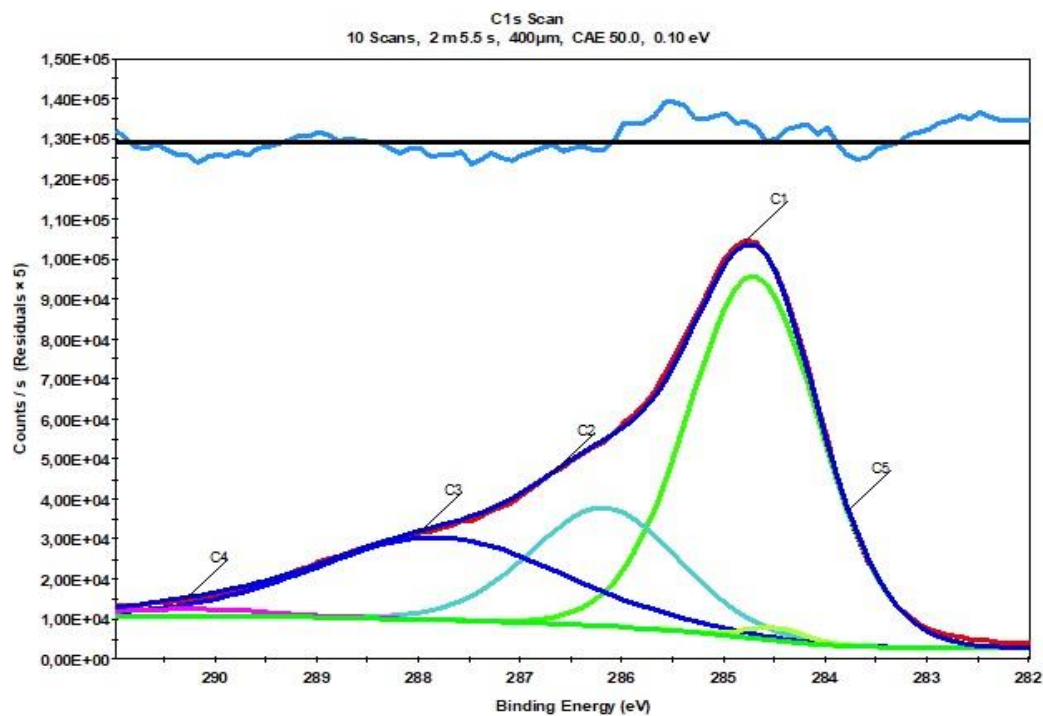


Figure 3. The C1s peaks in the XPS spectra of GO after treatment

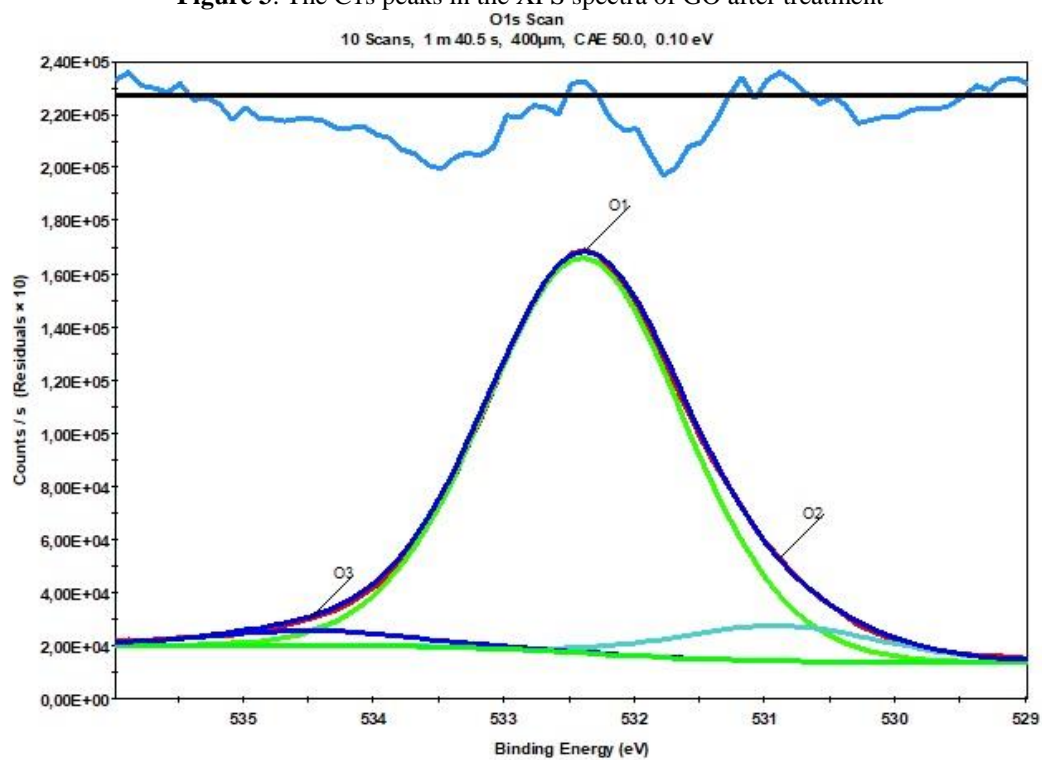


Figure 4. The O1s peaks in the XPS spectra of GO without treatment

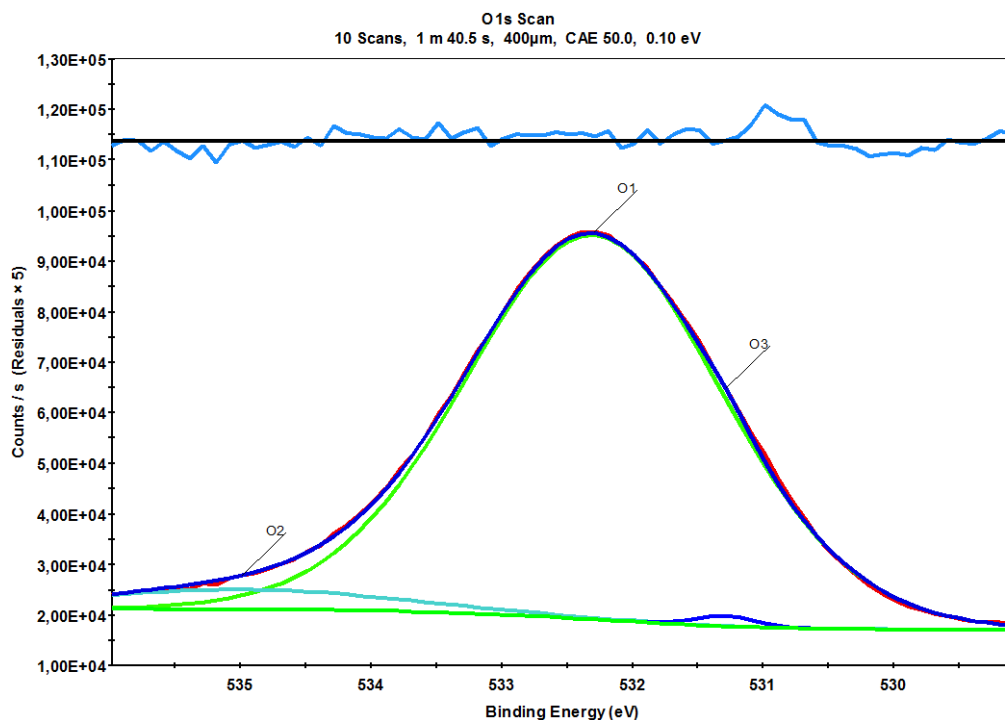


Figure 5. The O1s peaks in the XPS spectra of GO after treatment

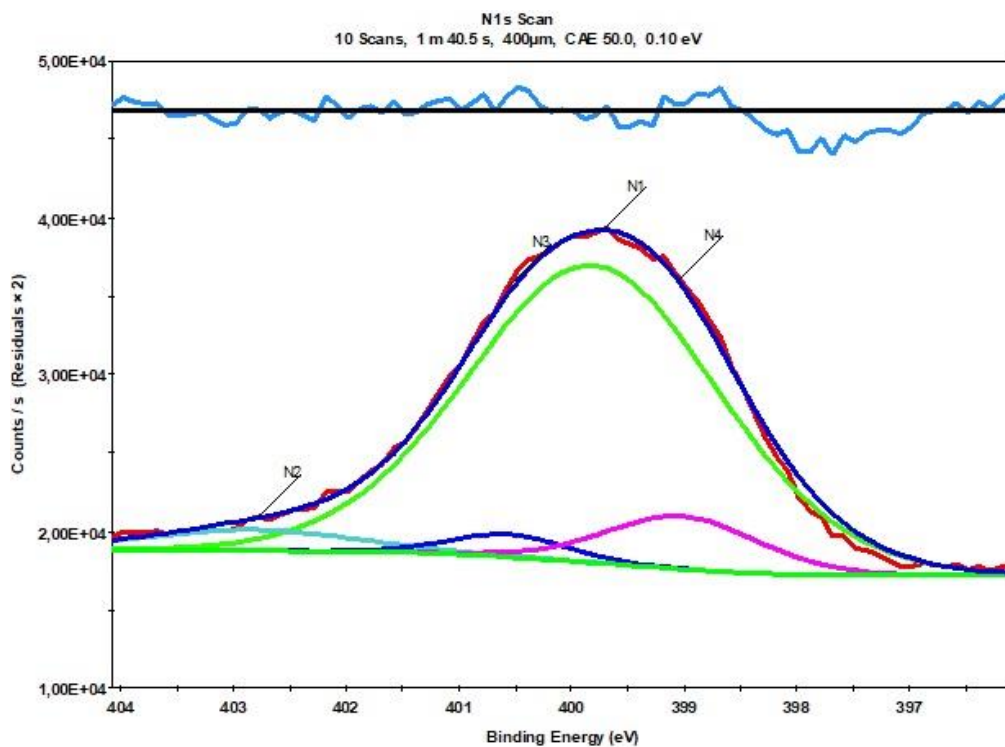


Figure 6. The N1s peak in the XPS spectra of GO after nitrogen glow discharge plasma

Conclusions. In summary, a fast, environmentally friendly method for the N-functionalization of GO using nitrogen glow discharge plasma was realized. Two samples were prepared and tested. The initial sample of graphene oxide and the sample treated with nitrogen glow discharge plasma with an irradiation dose of 1.5×10^{16} Ions/cm². The structure and morphology of the GO surface were studied using Raman spectroscopy and SEM. Graphene oxide has been successfully functionalized with nitrogen in a glow discharge plasma. The incorporation of nitrogen into GO results in the formation of three different N-bonded species. As a result, after treatment with nitrogen glow discharge plasma, the nitrogen content increased by almost 10 times. Moreover, irradiation leads to a decrease in the oxygen content, which has a significant effect on the structure and electronic properties of functionalized sample.

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References

1. D. Sahu, H. Sutar, P. Senapati, R. Murmu, D. Roy, Graphene, graphene-derivatives and composites: Fundamentals, synthesis approaches to applications, *Journal of Composites Science*. 5 (2021). <https://doi.org/10.3390/jcs5070181>.
2. H.P. Zhou, X. Ye, W. Huang, M.Q. Wu, L.N. Mao, B. Yu, S. Xu, I. Levchenko, K. Bazaka, Wearable, Flexible, Disposable Plasma-Reduced Graphene Oxide Stress Sensors for Monitoring Activities in Austere Environments, *ACS Applied Materials and Interfaces*. 11 (2019) 15122–15132. <https://doi.org/10.1021/acsami.8b22673>.
3. M. Don, S. Lakshad, J. Kim, S. Woon, J. Lee, Journal of Science : Advanced Materials and Devices Highly efficient two-step nitrogen doping of graphene oxide-based materials in oxygen presence atmosphere for high-performance transistors and electrochemical applications, *Journal of Science: Advanced Materials and Devices*. 7 (2022) 100481. <https://doi.org/10.1016/j.jsamd.2022.100481>.
4. M. Mohai, K. László, I. Bertóti, Reduction and covalent modification of graphene-oxide by nitrogen in glow discharge plasma, *Surface and Interface Analysis*. 50 (2018) 1207-1212. <https://doi.org/10.1002/sia.6411>.
5. R. Ikram, B.M. Jan, S.A. Pervez, V.M. Papadakis, W. Ahmad, R. Bushra, G. Kenanakis, M. Rana, Recent advancements of n-doped graphene for rechargeable batteries: A review, *Crystals*. 10 (2020) 1-27. <https://doi.org/10.3390/cryst10121080>.
6. K. Kuanyshebekov, K. Akatan, S.K. Kabdrakhmanova, R. Nemkaeva, M. Aitzhanov, A. Imasheva, Kairatuly, Synthesis of graphene oxide from graphite by the hummers method, *Oxidation Communications*. 44 (2021) 356-365.

Additional references

7. A.M. Ilyin, Computer Simulation of Radiation Defects in Graphene and Relative Structures, (2010).
8. A.M. Ilyin, N.R. Guseinov, I.A. Tsyganov, R.R. Nemkaeva, Computer simulation and experimental study of graphane-like structures formed by electrolytic hydrogenation, *Physica E: Low-Dimensional Systems and Nanostructures*. 43 (2011) 1262–1265. <https://doi.org/10.1016/j.physe.2011.02.012>.
9. Q. Lian, Z. Uddin, D. Dianchen, M.E. Zappi, D. Lord, B. Fortela, R. Hernandez, Chemosphere The effects of carbon disulfide driven functionalization on graphene oxide for enhanced Pb (II) adsorption: Investigation of adsorption mechanism, *Chemosphere*. 248 (2020) 126078. <https://doi.org/10.1016/j.chemosphere.2020.126078>.
10. A. Heterogeneous, E. Transfer, Nitrogen-Doped Graphene: The Influence of Doping Level on the Charge-Transfer Resistance and Apparent Heterogeneous Electron Transfer Rate, (2020).
11. M. Gijare, S. Chaudhari, S. Ekar, A. Garje, Reduced Graphene Oxide Based Electrochemical Nonenzymatic Human Serum Glucose Sensor, *ES Materials and Manufacturing*. 14 (2021) 110–119. <https://doi.org/10.30919/esmm5f486>.
12. A. Abu-Nada, A. Abdala, G. McKay, Isotherm and kinetic modeling of strontium adsorption on graphene oxide, *Nanomaterials*. 11 (2021) 1–11. <https://doi.org/10.3390/nano11112780>.
13. V.R. Moreira, Y.A.R. Lebron, M.M. da Silva, L.V. de Souza Santos, R.S. Jacob, C.K.B. de Vasconcelos, M.M. Viana, Graphene oxide in the remediation of norfloxacin from aqueous matrix:

- simultaneous adsorption and degradation process, *Environmental Science and Pollution Research*. 27 (2020) 34513–34528. <https://doi.org/10.1007/s11356-020-09656-6>.
14. L. Ouyang, J. Xiao, H. Jiang, S. Yuan, Nitrogen-doped porous carbon materials derived from graphene oxide/melamine resin composites for CO₂ adsorption, *Molecules*. 26 (2021). <https://doi.org/10.3390/molecules26175293>.
 15. S. Mahalingam, M. Durai, C. Sengottaiyan, Y.-H. Ahn, Effective Chemical Vapor Deposition and Characterization of N-Doped Graphene for High Electrochemical Performance, *Journal of Nanoscience and Nanotechnology*. 21 (2021) 3183–3191. <https://doi.org/10.1166/jnn.2021.19355>.
 16. H. Xu, L. Ma, Z. Jin, Nitrogen-doped graphene: Synthesis, characterizations and energy applications, *Journal of Energy Chemistry*. 27 (2018) 146-160. <https://doi.org/10.1016/j.jechem.2017.12.006>.
 17. Y.P. Lin, Y. Ksari, D. Aubel, S. Hajjar-Garreau, G. Borvon, Y. Spiegel, L. Roux, L. Simon, J.M. Themin, Efficient and low-damage nitrogen doping of graphene via plasma-based methods, *Carbon*. 100 (2016) 337-344. <https://doi.org/10.1016/j.carbon.2015.12.094>.
 18. E. Seliverstova, N. Ibrayev, E. Menshova, E. Alikhaidarova, Laser modification of structure and optical properties of N-doped graphene oxide, *Materials Research Express*. 8 (2021) 0-7. <https://doi.org/10.1088/2053-1591/ac31fc>.
 19. Y. Wang, F. Yu, M. Zhu, C. Ma, D. Zhao, C. Wang, A. Zhou, B. Dai, J. Ji, X. Guo, N-Doping of plasma exfoliated graphene oxide: Via dielectric barrier discharge plasma treatment for the oxygen reduction reaction, *Journal of Materials Chemistry A*. 6 (2018) 2011-2017. <https://doi.org/10.1039/c7ta08607e>.
 20. M. Mohai, I. Bertóti, Modification of graphene-oxide surface in nitrogen and argon glow discharge plasma, *Surface and Interface Analysis*. 48 (2016) 461-464. <https://doi.org/10.1002/sia.5929>.
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