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# Obtaining of Graphene Oxide by Spray-dryer Method

**Natia Jalagonia, Tinatin Kuchukhidze, Nino Darakhvelidze, Tamar Archuadze, Leila Kalatozishvili**

Ilia Vekua Sukhumi Institute of Physics and Technology

## ABSTRACT

Graphene and the composites and nanocomposites based on it are considered to be the most advanced materials today. Using it, it is possible not only to improve the properties of existing materials, but also to obtain completely new materials. For the last few years, work on graphene has been actively underway, resulting in improved materials, new technologies and the development of sensor technology. However, it should be noted that the synthesis of graphene with an ideal structure is a rather difficult and costly process, which is why it is being replaced by graphene oxide (GO) structures.The goal of our work was to obtain graphene oxide by the most common intercalation method, which is proposed in the literature and takes place in two stages. The next stage of the research was obtaining of graphene oxide corrugated granules by simultaneous spray-dryer method, for which Lab Granulator was used. We observed, that during the granulation process various size layers of GO arise. Size of granules ranged from ~5 nm to 500 nm. Above mentioned method gives the possibility to scalable produce defined size corrugated granules of GO. The identification and structural-morphological study of the obtained materials was carried out by XRD, SEM, UV and Raman spectral methods.

**Key words:** Graphene oxide, Intercalation, Corrugate, Granulation

## INTRODUCTION

With the beginning of the new century, the development of nanotechnologies became a decisive task of scientific research, and carbon turned out to be one of the principal directions of this concept, due to the unique property of its atoms - to form a long chain (catenation) and along with that to include other atoms and groups of atoms.

In the history of nanotechnologies, the discovery of carbon nanostructures: fullerenes and carbon nanotubes at the end of the 20th century, and the method of obtaining graphene in the 21st century [1] were most important. In 2010, among the the Nobel Prize laureates in Physics, Konstantin Novoselov and Andre Geim, from the groups of scientists from the University of Manchester, who discovered graphene in 2004, were named [2,3].

Graphene, the world's thinnest material, is an organic matrix consisting of hexagons with carbon atoms on the vertices [4]. Since its discovery, many studies have been focused on new ways of obtaining this material, its physical and chemical properties, and the manufacture of new graphene-based nanomaterials. However, it should be noted that the synthesis of graphene with an ideal structure is a rather difficult and costly process, which is why it is being replaced by graphene oxide and reduced graphene oxide structures [5,6].

The term **graphene oxide** refers to graphene particles that have molecules or functional groups attached to the edge or carbon chain, such as: hydroxyl, phenol, carboxyl, carbonyl, aryl, ether, phosphorous-bearing, etc. Unlike graphene, carbon in graphene oxide is in $sp^3$ hybridization and contains a large number of oxygen-containing groups, which allows it to be functionalized [7].

Graphene oxide is an excellent platform for obtaining both graphene and reduced graphene oxide and their chemically (covalently) modified materials. Graphene oxide itself is considered as graphene that has been modified with a set of oxygen-containing groups capable of replacing organic or inorganic functional groups. Such covalent modifications change both its electronic structure and adsorption properties and are widely used in sensors [8,9].

Graphene oxide, due to its layered structure, is well dispersed in water and polar and non-polar organic solvents (ethylene glycol, dimethylformamide, M-methylpyramidon, and tetrahydrofuran).

There are four principal ways to synthesize graphene oxide: that of Staudenmaier, Hoffmann, Brodie and Hummers; researchers are, however, trying to obtain a product of stable quality with less cost and minimal processing.

## MATERIALS, SYNTHESIS AND METHODS

*Methods:* In the i work, several advanced material characterisation equipment was used.

The X-ray diffraction analysis of the synthesized materials were carried out on DRON-3M.

The Raman spectroscopy analysis was done on a Witec UHTS 300, using a 532 nm laser with 1.5 mW power intensity under the conditions: filler single spectra, magnification: 50x, integration time 0.5 s; 532 nm excitation laser at room temperature.

Optical absorption spectra of Graphene oxide solution were taken from an ultraviolet visible spectrophotometer (UV, Shimadzu UV-3600).

An SD-1000 laboratory spray granulator was used for granulation, particle size control and other.

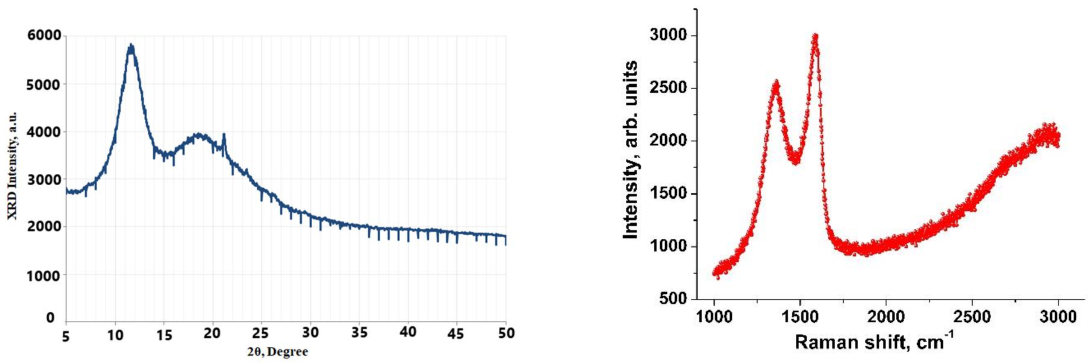
The Scanning Electron Microscope (SEM) Sigma 300 (Zeiss) with resolution 1 nm, was used for analysis of morphology.

**Synthesis of graphene oxide -** Synthesis of graphene oxide was conducted by modified Hummers method. 500 ml flask placed into a water bath (30-35°C), 2 g natural graphite was added into a mixture of 50 ml 98% $H_2SO_4$ and 6 g $KMnO_4$ and the solution was stirred during 1 h. Then temperature increased to 70°C and stirred during 1 h, after this added 200 ml $H_2O$ and 20 mL 30 % $H_2O_2$. Obtained graphene oxide suspension was filtered, washed and centrifuged to removal the waste graphite. Obtained product was dispersed in water by sonication. Resulting stable suspensions of graphene oxide was granulated by spray-dryer method for preparing of corrugated granules.

**Granulation of graphene oxide** -The reduced graphene oxide suspension was mixed on a magnetic stirring and delivered by a peristaltic pump to the granulation zone at a speed 10-20 ml/min. The granulation zone temperature is kept within 40-150˚C. The suspension was dispersed by the air compressed up to 3 atmospheres. The produced granules are collected in a receiver, and for final removal of the solvent, it was additionally dried in the vacuum oven.

## RESULTS AND DISCUSSION

The goal of our work was to obtain graphene oxide by the most common intercalation method, which is proposed in the literature and takes place in two stages, as follows: 6 g of graphite taken for synthesis (pre-activated or pyrolytic) is added to 50 ml of concentrated sulfuric acid and water bath, (t=27-35$^{o}$C ) under mechanical stirring, potassium permanganate is added in small portions during 1 hour. After raising the temperature to 70 $^{0}$C in the water bath, 100 ml of distilled water and another 100 ml after 30 minutes of removing from the stirrer are added. After adding 20 ml of hydrogen peroxide, the resulting mixture turns yellowish-golden, and after filtering and washing in a centrifuge, we get a brown-color 6% suspension of graphene oxide. Drying is carried out at a low (50-70 $^{0}$C) temperature.

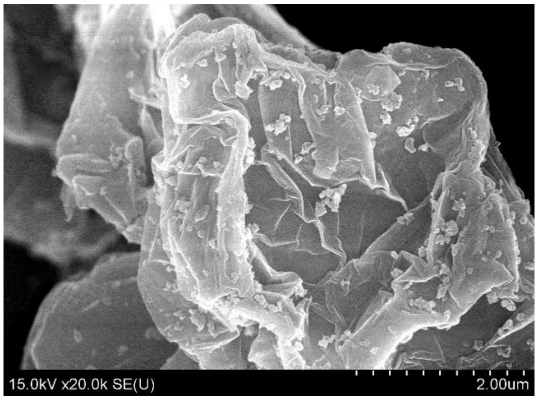



a b

Fig. 1. XRD (a) and Raman (b) of graphene oxide

In Figure 1a, a peak at 10$^{0}$ is observed which shows the presence of GO. Whereas the Raman spectroscopy results in Figure 1b show a “D” peak at 1590 cm$^{-1}$ and a “G” peak at 1350 cm$^{-1}$, which confirmed the lattice deformation. In the UV spectra (Figure 2b), the main peak at 230nm and the shoulder peak at 300nm stand for π-π* transitions of C=C bond from graphitic carbon of GO and n-π* transitions of C=O bond from oxidized carbon of GO respectively.

The next stage of the research was obtaining of graphene oxide by spray-dryer method. Graphene oxide microspheres were obtained by this method. Its morphology was studied By SEM (Figure 2a) and UV spectroscopy. The images proves that different size, corrugated granules of the graphene oxide were obtained. Graphene oxide has excellent features such as large surface area, high stability, and layered structure. Therefore, the graphene oxide granules obtained by the above-mentioned method make their homogenization in different matrices (Polymer, ceramic and etc.) much easier.



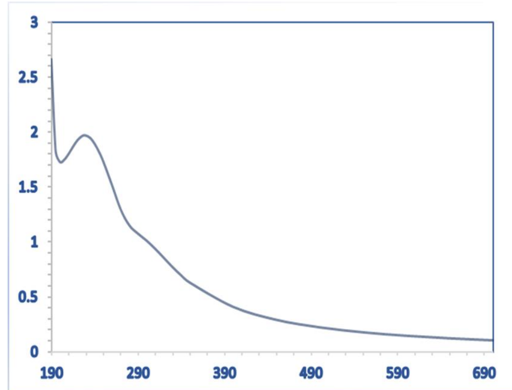




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Fig. 2. SEM (a) and UV (b) of graphene oxide

## Conclusion

Graphene and its derivatives are promising materials used as fillers in polymers, ceramics, etc. The field of application of composites containing graphene structure is very wide. The present work deals with the synthesis of graphene oxide granules. The obtained materials identification and structural-morphological characterization were undertaken using XRD, SEM, UV and Raman spectral methods. Simultaneous spray-dryer method gives the possibility to scalable produce defined size corrugated granules of GO.

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# გრაფენის ოქსიდის მიღება გაფრქვევა-გაშრობის მეთოდით

**ნათია ჯალაღონია, თინათინ კუჭუხიძე, ნინო დარახველიძე, თამარ არჩუაძე, ლეილა კალატოზიშვილი**

სოხუმის ილია ვეკუას ფიზიკა-ტექნიკის ინსტიტუტი

**აბსტრაქტი**

გრაფენი და მასზე დაფუძნებული კომპოზიტები და ნანოკომპოზიტები დღეს ყველაზე მოწინავე მასალებად ითვლება. მისი გამოყენებით შესაძლებელია არა მხოლოდ არსებული მასალების თვისებების გაუმჯობესება, არამედ სრულიად ახალი მასალების შექმნა. ბოლო რამდენიმე წლის განმავლობაში გრაფენზე მუშაობა აქტიურად მიმდინარეობს, რის შედეგადაც გაუმჯობესდა მასალები, ახალი ტექნოლოგიები და განვითარდა სენსორული ტექნოლოგია. თუმცა, უნდა აღინიშნოს, რომ გრაფენის იდეალური სტრუქტურის სინთეზი საკმაოდ რთული და ძვირადღირებული პროცესია, რის გამოც ხდება მისი ჩანაცვლება გრაფენის ოქსიდის სტრუქტურებით. ჩვენი სამუშაოს მიზანი იყო გრაფენის ოქსიდის მიღება ყველაზე გავრცელებული ინტერკალაციის მეთოდით, რომელიც შემოთავაზებულია ლიტერატურაში და მიმდინარეობს ორ ეტაპად. კვლევის შემდეგი ეტაპი იყო გრაფენის ოქსიდის გრანულების მიღება ერთდროული გაფრქვევა-გაშრობის მეთოდით, რისთვისაც გამოყენებული იქნა ლაბორატორიული გრანულატორი. ჩვენ დავაკვირდით, რომ გრანულაციის პროცესში წარმოიქმნა გრაფენის ოქსიდი სხვადასხვა ზომის ფენები. გრანულების ზომა მერყეობდა ~5 ნმ-დან 500 ნმ-მდე. ზემოაღნიშნული მეთოდი გრაფენის ოქსიდი გოლფრირებული გრანულების მასშტაბირებადი წარმოების შესაძლებლობას იძლევა. მიღებული მასალების იდენტიფიკაცია და სტრუქტურულ-მორფოლოგიური შესწავლა განხორციელდა რენდეგნით, ელექტრონული მიკროსკოპით, ულტრაიისფერი და რამანის სპექტრული მეთოდებით.

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