Bulgarian Chemical Communications, Volume 58, Special Issue A (pp. 26-30) 2026 DOI: 10.34049/bcc.58.A.SN-05

Direct synthesis of graphene by using combined electrolysis and ultrasonic methods

D. Georgiev, I. Markovska, F. Yovkova*, S. Kozarev

Burgas State University “Prof. Dr. Assen Zlatarov”, 1 Prof. Yakimov Blvd., Burgas, 8010, Bulgaria

Received: July 02, 2025; Revised: November 26, 2025

Graphene is a novel nanomaterial that possesses many amazing characteristics. It is considered as a next-generation conductive material with the potential to be used for obtaining of electrodes for supercapacitors. In the present paper, monolayer graphene was synthesized through simultaneous application of electrolysis and ultrasound. High-purity finely dispersed graphite was used as a precursor. Graphene was obtained *via* a combination of chemical and physical treatment, with sulfuric acid serving as the electrolyte. The acid loosens the weak van der Waals bonds, and together with the acoustic action of ultrasound, contributes to the cleavage of the individual graphene layers.

Keywords: Graphene, Ultrasound, Electrolysis

INTRODUCTION

Graphene is a two-dimensional atomic-scale material made of a single layer of carbon atoms. The latter have a high level of cohesion through hybridization bonds sp^2 and are arranged in a uniform surface, slightly undulating, with appearance similar to a honeycomb lattice because of its hexagonal configuration [1]. Graphene is an allotropic form of carbon, as graphite or diamond. One millimeter of graphite contains three million layers of graphene [1]. This is the first stand-alone material with a 2D structure, which has unique properties. These properties make it extremely interesting both for basic science and in applied aspect. Until recently, it was thought that planar graphene could not exist in the free state because it was unstable with respect to the formation of curved structures such as soot, fullerenes, and nanotubes [2-4].

Graphene possesses many amazing characteristics. Its electron mobility is 100 times faster than that of silicon. Graphene conducts heat 2 times better than diamond; at the same time its electrical conductivity is 13 times better compared to copper. This material absorbs only 2.3% of reflected light; it is impervious so that even the smallest atom (helium) can't pass through a defect-free monolayer graphene sheet [5].

Graphene is obtained from graphite by separating the planar networks that form the hexagonal crystal lattice of graphite. Actually, graphite consists of many flat layers of graphene sheets (Fig. 1 a, b).

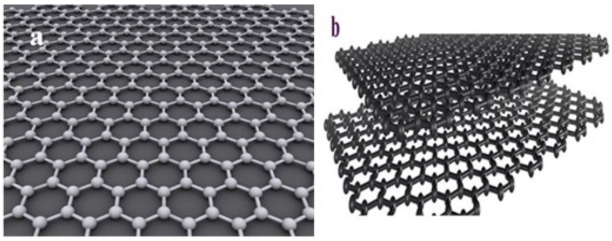

Fig. 1. Single-layer (a) and double-layer (b) structure of graphene.

There are various methods to synthesize graphene and its derivatives. Effective ways for detachment of graphene planes are by high-voltage discharge, or by electron beam or laser sputtering in helium medium [6, 7].

The main methods of graphene preparation are: mechanical exfoliation, chemical exfoliation, CVD (chemical vapor deposition), epitaxial growth, pyrolysis, etc. [8-12]. Hummers' method [13] was developed in 1958 as a faster and more efficient method of preparation of graphitic oxide. In recent years many teams are looking into ways of using graphitic oxide as a precursor to mass production of graphene.

The main difficulties in graphene preparation are related to the fact that it is quite difficult to obtain a significant amount of high-quality sample. The method of Novoselov (micromechanical exfoliation of graphite layers) gives neither high-quality product, nor high yield. It is necessary to overcome the energy of van der Waals interactions between the layers without disrupting the first, second and the other layers below, which is very difficult.

Graphene offers many opportunities for electronics [14-19]. At present, graphene is extensively studied with a view to its use in the

---

* To whom all correspondence should be sent:
E-mail: *fila_03@abv.bg*

production of supercapacitors able to be quickly charged and store higher amounts of electric energy [14, 15]. Lithium-ion batteries improved with graphene can be used in electricity-driven vehicles, as well as in smartphones, laptops and tablets with significantly smaller weight [16]. Intense efforts are devoted to the development of graphene sensors (gas, bio and light) [19]. In this respect, the present paper reports for preparation of graphene from high-purity finely dispersed graphite by simultaneously applying electrolysis and ultrasound. Graphene was obtained *via* a combination of chemical and physical treatments, with sulfuric acid serving as the electrolyte. The acid weakens the van der Waals interactions, and together with the ultrasonic acoustic effects, facilitates the exfoliation of individual graphene layers.

EXPERIMENTAL

Materials

High-purity (99.9%) finely dispersed graphite (GO) was used as a precursor for graphene synthesis. The particle size of the graphite powder was below 200 µm. The electrical resistance of pristine graphite was 11×10^{-8} Ω m. Sulfuric acid (H_2SO_4), potassium hydroxide (KOH) and deionized water were also used (Fig. 2).

Fig. 2. Initial graphite powder

Methods

The obtained graphene was mainly characterized using Raman spectroscopy and Fourier transform infrared (FT-IR) spectroscopy.

- *Raman spectroscopy.* The Raman spectra were obtained using LabRAM HR Visible Raman spectrometer. For excitation the 633 nm line of a He-Ne laser was used. To decrease the possible local overheating, the used laser power on the sample surface was reduced to 360 µW. An objective X50 was used both to focus the incident laser light and to collect the scattered light in backscattering geometry. The diameter of the laser spot on the sample surface was about 3 µm. At least three spectra at different arbitrary chosen spots from each sample were collected. The investigated spectral range was 900 cm^{-1} ÷3500 cm^{-1}. The most intense lines in the spectra (namely, D, G, D’ and 2D) were fitted with Lorentzians and the line parameters (as well the intensity line ratios) were calculated.

The method used in the present work involves simultaneous application of ultrasound and electrolysis. Finely ground graphite (> 99%) which burns without residue was used as a precursor for the synthesis of graphene. In a beaker, 200 ml deionized water were placed, then 8 ml of 4N H_2SO_4 and 5 g of pure finely dispersed graphite G0 were added and the mixture was well homogenized. The beaker with the sample was placed in an ultrasonic bath filled about 2/3 with deionized water (Fig. 3).

Fig. 3. Experimental setup for combined ultrasonic treatment and electrolysis.

The experiment was carried out in the ultrasonic bath at room temperature for 4 h. In our case, the sulfuric acid plays the role of a liquid medium for propagation of the acoustic waves while, according to the literature review, the media used for this purpose by other authors were ethyl alcohol, acetone, heptane and other liquids.

Table 1 shows the compositions synthesized and the experimental conditions.

Table 1. Compositions synthesized and experimental conditions

Sample №	G_0, g	4N H_2SO_4, ml	H_2O, ml	Electrolysis, min	Ultrasound, min	Current magnitude, A	Voltage, V
GE1	5	8	200	5	30	1	5.6
GE2	5	8	200	10	30	1	5.6
GE3	5	8	200	15	30	1	5.6
GE4	5	8	200	5	30	3.1	10.6
GE5	5	8	200	30	30	3.1	10.6

Electrolysis and ultrasound were simultaneously applied. Fig. 3 shows a picture of the experimental installation with combined application of ultrasound and electrolysis.

Graphite electrodes were placed in a beaker (Fig. 4). For samples GE1, GE2 and GE3, the electrodes were plate-shaped while for samples GE4 and GE5 they were cylindrical. The distance between the electrodes was 10 mm.

Fig. 4. Photograph of the experimental layout for carrying out the electrolysis

The electrolysis and the ultrasonic treatment took place simultaneously. The experiments were carried out at a temperature of 17 – 30°C and ultrasound frequency of 40 kHz. The samples were then filtered and the solid residue was dried at 110°C for 5 h.

The electrolyte used was an aqueous solution of H_2SO_4. Sulfuric acid dissociates according to the equation: $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$. By the application of electric field in the electrolyte, the positive ion H^+ was deposited on the cathode while the negative one SO_4^{2-} – on the anode. The following primary processes took place on the cathode and on the anode:

- on the cathode: $2H^+ + 2e^- = H_2\uparrow$
- on the anode: $SO_4^{2-} - 2e^- = SO_4$

The neutral radical SO_4 is extremely active and cannot exist in free state. It reacts with water and a secondary reaction occurs on the anode:

$$2SO_4 + 2H_2O = 2\ H_2SO_4 + O_2\uparrow$$

As a result, one molecule of sulfuric acid has returned to the solution and one molecule of water has released oxygen on the anode and hydrogen on the cathode.

RESULTS AND DISCUSSION

Characteristics of graphene

- *Raman spectroscopy*

Raman spectroscopy was used to obtain structural information of the prepared graphene. Fig. 5 shows the Raman spectrum of sample GE1 where the major peaks of graphene can be observed. The carbon material displays distinctive Raman peaks known as D-, G- and 2D-peaks at approximately 1350, 1580 and 2700 cm^{-1}, respectively [20]. In our case (Fig. 5) these lines are at 1337, 1578 and 2669 cm^{-1}, respectively. The intensity ratio of 2D-peak to G-peak (I_{2D} /I_G) can be used to evaluate the quality of graphene. A large I_{2D} /I_G and insignificant D-peak indicate the high quality of graphene [21].

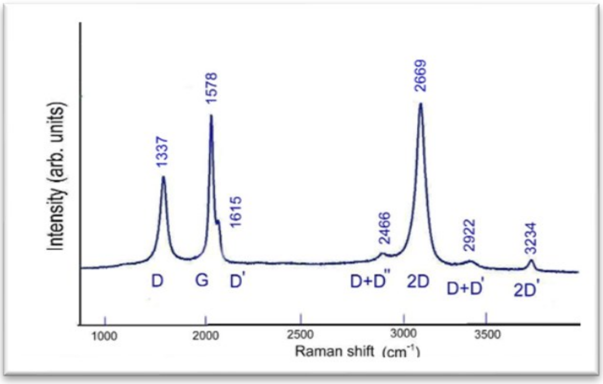

Fig. 5. Raman spectrum of sample GE1

As shown in Fig. 5, the spectrum of sample GE1 has all characteristic peaks of graphene, such as D, G, 2D and D+G bands. Only lines, typical for the graphene-like samples, are visible. The sample GE1 has I_{2D}/I_G ratio > 1 and the smallest width of the lines, so it can be characterized as a sample of high-quality graphene. For comparison, in Fig. 6 the Raman spectra of pure graphene according to Calizo *et al.* [22] (a) and Wang *et al.* [23] (b) are given.

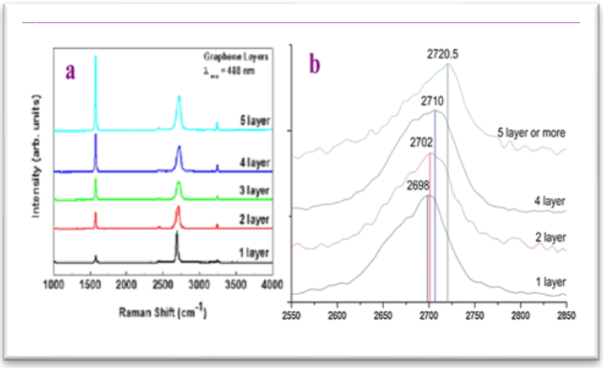

Fig. 6. Raman spectra of graphene according to: a) Calizo *et al.* [22] and b) Wang *et al.* [23]

It is known that the frequency shift and the shape change of the Raman peak at the 2D band can be used to distinguish the number of layers in graphene samples [23, 24]. Comparing our result from Fig. 5 with the literature data presented in Fig. 6 it can be seen that the spectra obtained by us correspond to monolayer graphene. In our samples, therefore, using the change in the shape and frequency of the 2D band peak located at 2669 cm^{-1} shown in Fig. 5, we can identify sheets consisting of a single layer and two layers of graphene, according to Calizo *et al.* [22] and Wang *et al.* [23].

- *Infrared spectroscopy (FT-IR)*

Fourier transform infrared (FT-IR) spectra provide information about the functional groups in a sample. FT-IR spectra of samples GE3, GE4 and GE5 are shown in Fig. 7.

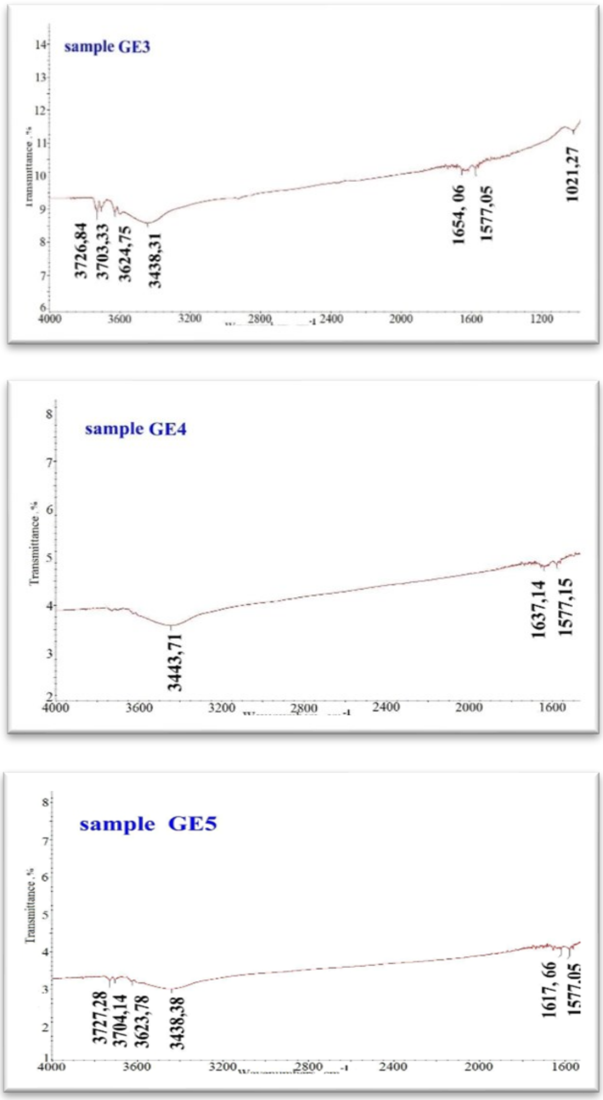

Fig. 7. IR spectra of samples GE3, GE4 and GE5

The FT-IR spectrum of sample GE3 displays absorption bands at 3726.84 cm^{-1}, 3703.33 cm^{-1}, 3624.75 cm^{-1}, 3438.31 cm^{-1}, 1654. 06 cm^{-1}, 1577.05 cm^{-1} and 1021.27 cm^{-1}. The FT-IR spectrum of sample GE4 displays absorption bands at 3443.71 cm^{-1}, 1637.14 cm^{-1} and 1577.15 cm^{-1}. The FT-IR spectrum of sample GE5 displays absorption bands at 3727.28 cm^{-1}, 3704.14 cm^{-1}, 3623.78 cm^{-1}, 3438.38 cm^{-1}, 1617, 66 cm^{-1}, 1577.05 cm^{-1}.

The results obtained from the FT-IR spectra shown in Fig. 7 indicate the presence of large peaks for all samples around 3400 – 3440 cm^{-1} corresponding to O–H vibrations.

The FT-IR spectra of samples GE3 and GE5 display absorption bands in the range of 3800 to 3600 cm^{-1} due to O-H stretching and hydrogen-bonded OH.

The absorption bands with maxima at 1654.06 cm^{-1}, 1637.14 cm^{-1} and 1617.66 cm^{-1} are characteristic of the O–H stretching of adsorbed water, as well as for skeletal vibrations from the rest which did not react graphitic domain. The vibrations can be attributed to the C=C bond**.** The peak around 1550 cm^{-1} is characteristic of the graphene double bond (v C = C) [25]. In our case it is observed at 1577.05 cm^{-1} (for GE3), 1577.15 cm^{-1} (for GE4) and 1577.05 cm^{-1} (for GE5). The new observed band at 1021.27 cm^{-1} can be assigned to the symmetric and asymmetric stretching modes of $-SO_3H$ functional groups and demonstrates the presence of sulfonic acid groups in sample GE3, as a result of pre-treatment of the graphite precursor with sulfuric acid [25–28].

The simplest spectrum observed was that for sample GE4. For sample GE4, the electrolysis was carried out for 5 min, for GE3 – for 15 min and for GE5 – for 30 min (Table 1). The results presented in Fig. 7 indicate that the duration of electrolysis has a major effect on bond formation. For the sample with the shortest duration of electrolysis (GE4), the smallest amounts of side bonds, as well as interaction with radicals from the dissolution of the "solvent" H_2SO_4. were observed.

CONCLUSIONS

Profound studies were carried out on the synthesis of a new nanomaterial – graphene by using combined electrolysis and ultrasonic methods. Our particular contribution can be described as follows:

- A combination of chemical and physical impacts on graphite as a precursor (> 99%) was applied for the preparation of graphene.
- Raman spectra proved that monolayer graphene was synthesized.
- The results obtained from the IR spectra indicated that the duration of electrolysis has a major effect on bond formation. For the sample with the shortest duration of electrolysis (GE4), the smallest amounts of side bonds were observed.
- The present work shows that high-quality graphene samples can be obtained by an inexpensive and easily scalable electrochemical process.

REFERENCES

1. https://www.graphenano.com/en/what-is-graphene/
2. A. Geim, K. Novoselov, *Nature Mater.*, **6**, 183 (2007).

3. V. Mohan, K. Lau, D. Hui, D. Bhattacharyya, *Composites Part B,* **142**, 200 (2018).
4. A. Neto, F. Guinea, N. Peres, *Phys World*, **19** (11), 33 (2006).
5. https://www.nanowerk.com/what_is_graphene.php
6. A. Gusev, Nanomaterials, Nanostructures, Nanotechnologies, Fismmatt, Moscow, 2007, p. 416.
7. A. Gusev, A. Rempel, Nanocrystalline Materials, Cambridge, 2004, p. 351.
8. D. Sreedhar, S. Devireddy, V. Veeredhi, *Materials Today*, **5**, 3403 (2018).
9. J. Zhang, T. Tian, Y. Chen, Y. Niu, J. Tang, A. L. Qin, *Chemical Physics Letters,* **591**, 78 (2014).
10. S. Park, J. An, J. Potts, A. Velamakanni, S. Murali, *Carbon,* **49**, 3019 (2011).
11. I. Moon, J. Lee, R. Ruoff, H. Lee, *Nature Communications,* **73** (1), (2010). https://doi.org/10.1038/ncomms1067.
12. K. Narasimharao, G. Venkata Ramana, D. Sreedhar, V. Vasudevaro, *J. Material Sci. Eng*., **5**, 284 (2016). doi:10.4172/2169-0022.1000284.
13. W. Hummers Jr., R. Offeman, *Journal of the American Chemical Society,* **80** (6), 1339 (1958).
14. A. Yu, I. Roes, A. Davies, Z. Chen, *Appl. Phys. Lett.,* **96**, 253105 (2010) https://doi.org/10.1063/1.3455879.
15. C. Liu, Z. Yu, D. Neff, A. Zhamn, *Nano Lett*., **10** (12) 4863 (2010).
16. J. Li, Y. Zhang, T. Gao, J. Han, X. Wang, B. Hultman, P. Xu, Z. Zhang, G. Wu, B. Song, *Journal of Power Sources*, **378**, 105 (2018).
17. H. Kim, Y. Chung, E. Lee, S. Lee, K. Cho, *Adv. Mater*., **26** (20), 3213 (2014). https://doi.org/10.1002/adma.201305940.
18. H. Wang, A. Hsu, T. Palasios, *IEEE Microwave Magazine,* **13** (4), 114 (2012).
19. B. Zhan, C. Li, J. Yang, G. Jenkins, W. Huang, X. Dong, *Small*, **10** (20), 4042 (2014).
20. X. Lee, B. Hiew, K. Lai, S. Gan, S. Thangalazhy-Gopakumar, S. Rigbyet, *Journal of the Taiwan Institute of Chemical Engineers*, **98**, 163 (2019).
21. W. Li, C. Tan, M. Lowe, H. Abruna, D. Ralph, *ACS Nano*, **5** (3), 2264 (2011).
22. I. Calizo, I. Bejenari, M. Rahman, G. Liu, A. Balandin, *J. Appl. Physics*, **106**, (2009). DOI: 10.1063/1.3197065.
23. W. Wang, Y. Wang, Y. Gao, Y. Zhao, *J. of Supercritical Fluids*, **85**, 95(2014).
24. A. Gupta, G. Chen, P. Joshi, S. Tadigadara, P. Eklund, *Nano Letters*, **6**, 2667 (2006).
25. B. Ossonon, D. Belanger, *RSC Adv*. **7**, 27224 (2017).
26. D. Jiang, Q. Yao, M. McKinney, C. Wilkie, *Polym. Degrad. Stab*., **63**, 423 (1999).
27. J. Lu, Y. Li, S. Li, S. Jiang, *Sci. Rep.* **6**, 21530 (2016).
28. D. Johnston, D. Shriver, *Inorg. Chem.* **32**, 1045 (1993).