Sakarya University Journal of Science

ISSN : 2147-835X
Publisher : Sakarya University

Vol. 28, No. 2, 283-293, 2024
DOI: https://doi.org/10.16984/saufenbilder.1271095

Research Article

Morphological and Structural Characterization of Low-Cost Graphene Produced by Electrochemical Exfoliation Method

Tamer Güzel[1*], Yasemin İşlek[1], Oğuzhan Yıldız[2]

[1] Niğde Ömer Halisdemir University, Mechatronic Department, Niğde, Türkiye, tamerguzel7840@gmail.com, ymeric@ohu.edu.tr
[2] Niğde Ömer Halisdemir University, Electrical and Energy Department, Niğde, Türkiye, oguzhan.yildiz@ohu.edu.tr
* Corresponding Author

ARTICLE INFO

Keywords:
Exfoliation Graphene
Electrochemical Exfoliation
Graphene Nanosheet
Graphene Layer
Raman
XRD

Article History:
Received: 26.03.2023
Accepted: 26.12.2023
Online Available: 22.04.2024

ABSTRACT

The low-cost and mass production of graphene has gained importance in recent years. The electrochemical exfoliation method, one of the graphene production methods, is an efficient technique used to obtain low-cost-effective and large quantities of graphene nanosheets. Exfoliation parameters affect the properties of exfoliated graphene nanosheets. In this study, graphene production is fabricated by the method of exfoliation using electrolyte and voltage parameters. For this, a pen tip was used instead of pure platinum, which is very expensive, at the cathode. The structural research was done by X-ray diffraction spectroscopy (XRD), Raman spectroscopy and Fourier Transform Infrared Spectrometer (F-TIR). Morphological analyses were carried out by Scanning Electron Microscopy (SEM). The number of layers and crystallite of graphene layers were estimated. The obtained results were compared with the results of the other similar studies. Analysis results show that low-cost multilayer graphene can be produced by the electrochemical exfoliation method with the electrical parameters.

1.Introduction

Graphene is defined as two-dimensional (2D) honeycomb lattice, sp^2-hybridized carbon atoms with only ultra-thin sheet layer of carbon atoms (one-atom-thick) [1]. This material has many properties such as high conductivity and transparency [2-11]. Because of these unique properties, graphene has the potential to apply in many fields including nano electronics, space, nuclear, automotive, medicine and biomedical industrial areas [10, 12-14]. Also, it can be used in transparent conductive films, electronic circuits, sensors (chemical and biosensors), transparent and flexible electrodes for screens, and carbon-based materials such as energy storage devices [15-19]. Because of its widely application area of this material, the production of high amounts of graphene at low costs has gained significant importance.

Many techniques have been improved for graphene fabrication, some of these are micromechanical method, chemical vapor deposition (CVD), liquid-phase exfoliation, electrochemical exfoliation, chemical synthesis (Hummers Method), chemical reduction of graphene oxide and epitaxial growth on Silicon Carbide[20-25]. These techniques often require clean room, vacuum environments and high temperatures. On the other hand, some of these techniques required poisonous molecules(gases). So they are not suitable for serial production. The electrochemical exfoliation method, one of these production techniques that could be used at different temperatures, does not necessarily a special ambiance (such as a vacuum), is environment-friendly, and can be made for superior quality products.

This method is also appropriate for production in large quantities [26-28]. Because of these

Cite as: T. Güzel, Y. İşlek, Yıldız O. (2024). Morphological and Structural Characterization of Low-Cost Graphene Produced by Electrochemical Exfoliation Method, *Sakarya University Journal of Science,* 28(2), 283-293. https://doi.org/10.16984/saufenbilder.1271095

advantages, high quantities of graphene could be manufactured at a lower price using this technique. On the other hand, the electrochemical exfoliation system has two electrodes and an ionic liquid. Generally, one of these electrodes is a graphite used as a carbon source and the other is conductive material that is not affected by acidic ambiance [28].

Exfoliation parameters affect the features of exfoliated graphene nano sheets. In the literature; many researchers have carried out extensive work on lower-price and superior-quality graphene fabricated by electrochemical exfoliation of graphite. Coros showed a low-cost and simple way to produce graphene nano sheet by exfoliation of graphite rods. They explained that this method has many advantages, such as being able to control the oxidation degree of graphene with the applied voltage[28]. Petrovski et al obtained graphene using with electrolysis in sulfuric acid electrolytes. They developed a low cost method for high-yield production of graphene[29].

Wang et al investigated that highly efficient and a large amount synthesis of graphene by electrolytic exfoliation. They explained that the current preparation method can be scaled up for the mass production of graphene materials [30]. Sahoo et al reported that simple, fast and cost-effective graphene nanosheets can be obtained using electrochemical synthesis method. They also reported ionic liquid is a significant key factor in reducing imperfection and oxidation [30]. Munuera et al showed that pre-treatment with concentrated sulfuric acid is a powerful strategy to increase the anodic exfoliation efficiency of graphite foil in an aqueous electrolyte media. They announced that this easy way should help to make anodic exfoliation a more vying method for the mass production of graphene [31].

Zhou et al studied a large amount production of high-quality graphene by innovator electrochemical exfoliation at air-electrolyte interface. They reported that a novel electrochemical exfoliation method at the air-electrolyte interface to obtain the high-quality graphene with excellent yield from the graphite foil in $(NH_4)_2SO_4$ electrolyte [32]. Chen et al reported that nano clay helped the exfoliation of graphite for converting to superior-conducting graphene. They also reported that a sophisticated and cost-effective approach for manufacturing high-conductive graphene products was approved by nano clay-helped exfoliation of graphite rod in liquid electrolyte ambiance [33].

In recent years, interest in the synthesis methods of graphene production has been increased. Therefore, the characterization of graphene nanosheets produced using electrochemical electrolysis method has gained importance because of some advantages such as economic and environmentally friendly.

In this study, pristine graphene was produced using the electrochemical exfoliation method. This method is a very practical, environmentally friendly approach that does not require special rooms. Structural analysis was performed using X-Ray Diffraction Diffractometer, Raman Spectrometer and Fourier Transform Infrared Spectrometer. Morphology examination of the produced graphene was done using Scanning Electron Microscope. The obtained results were discussed in comparison with each other and similar other studies.

2. Experimental

2.1. Production of graphene nanosheets

In this study graphite rods and sulfuric acid (H_2SO_4) were mainly used. A commercially available 0.7mm (HB) pen tip was located as the counter electrode. The electrochemical exfoliation operations were done in (2)-electrode system. The graphite rod and pen tip were placed in 1M H_2SO_4 solution as shown in Figure 1A.

The electrochemical exfoliation process was started by applying voltage by DC power supply (+10 V) on the graphite electrode. The process was completed in about 4 minutes. After the exfoliation process, the deposited layers on the surface part of the electrolyte were gathered (Figure 1D). After 30 min of sonication, vacuum filtration was implemented with a 0.22 mm porous polyvinyl membrane filter. Finally, the sample was washed several times with deionized water to clean acid salts from the surface and desiccated at 80°C. According to the experimental observations, when the exfoliation process was finished (about 4 minutes), the layer expansion and the structural change were observed in the graphite in the form of pure rods (Figure 1B).

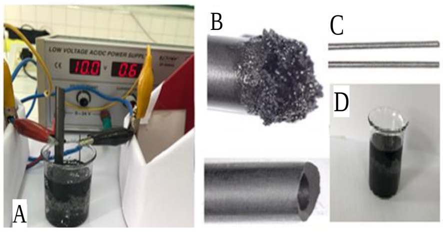

Figure 1. A- Experiment setup B- Image of the graphite rod before and after exfoliation C- Image of the pen tip before and after exfoliation D- The exfoliate products in suspension

Besides, any change in the structure of the pen tip used as counter electrode was not observed. (Figure 1C). The exfoliation product was analyzed in Niğde Ömer Halisdemir University Central Research Laboratory. Structural examination of the produced samples was done with the help of X-ray Diffraction Analyses (XRD), Raman Spectroscopy, and Fourier Transform Infrared Spectroscopy (F-TIR). In addition, the morphological research of the samples was done by Scanning Electron Microscope (SEM).

3. Results and Discussion

3.1 X-Ray diffraction

The XRD technique was used to examine the crystal structure of the product formed as a result of exfoliation with graphite. The XRD patterns of graphite and exfoliation products are shown in Figure 2. As shown in Figure 2A, there are four peaks in the graphite diffraction pattern (2θ) 26.57, 42.50, 44.57 and 54.57. These peaks are compatible with the reflection planes (h k l) 0 0 2, 1 0 0, 1 0 1 and 0 0 4 respectively. The graphite shows peaks centered at 26.52° corresponding to the 0 0 2 plane. On the other hand, the exfoliation product indicates peaks centered at 26.40° corresponding to the 0 0 2 plane but its peak is shorter and wider than the graphite peak.

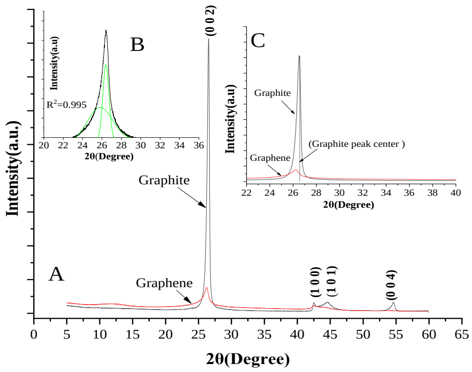

Figure 2. A- X-ray diffraction patterns of graphite and graphene B- Deconvoluted of the peak of the 2 0 0 plane of the graphene C- Comparison of graphite and graphene peak centers of the 0 0 2 plane

The reason for the shorter peak may be due to a reduction in the number of layers or a mixture of nanosheets having different number of layers [34]. It is clearly seen the situation at Figure 2B. According to that, when the 2 0 0 plane reflection angle is deconvolved, it can be seen that it actually consists of different nested peaks.

On the other hand, this indicates layers of stacked and corrugated graphene sheets [35]. These diffraction patterns are also indicative of the formation of multi-layer graphene nanosheets [36, 37]. In addition, it can be seen that the reflection angles relative to plane 0 0 2 shift at a lower angle after exfoliation. This shows an increase in the d space value and consequently a decrease in the number of layers (Figure 2C).

The reason of that is formation of CO_2 and CO gases between the layers of graphite due to the formation of oxygen gas with SO_4^{2-} ions and hydroxylation to the surface and edges of the graphene nanosheets. This may be another reason for increasing the interlayer spacing [36]. These results are compatible with the literature [29, 33, 38, 39]. According to these results, the product obtained by exfoliation was understood to be graphene. This demonstrates the success of the exfoliation process. On the other hand, to find the graphene layer, Debye-Scherrer (Eq. 1,2) and Bragg equations (Eq. 3) can be used [40].

$$L_a = \frac{k\lambda}{\beta Cos\theta} \quad (1)$$

$$n = \frac{L_a}{d} \quad (2)$$

$$d = \frac{n\lambda}{2Sin\theta} \quad (3)$$

where L_a is the crystallite size, λ is the wavelength of the laser, β is the width of the measured peak in half of the maximum (FWHM) in radians, k is shape factor (k=0.89), the angle θ is the angle of reflection of the plane 0 0 2 and n is the number of layers.

Table 1. The analysis results of XRD spectra

Sample	2θ (°)	d-spacing (Å)	L_a (nm)	Layers of number (n)
Graphite	26.52	3.35	14.71	66.47
Graphene	26.40	3.38	2.79	9

According to the Equation 1; the crystallite value of graphene were calculated as 2.79 nm [29]. In addition, the number of layers was found about 9 layers with the angle of 26.40° of the graphene, from Equation 2. Some parameters and calculated layers number for graphite and graphene are shown in Table 1. Since the shortening and expansion of the sharp peak decreases the crystallite value according to the Debye-Scherrer equation, this can be interpreted as graphene formation.

When examined in Figure 3B, it can be seen the peak of graphite at 44.57 degrees disappears after graphene formation. However, it can be seen the peak of graphite at 55.47 degrees is shortened and expanded after exfoliation in Figure 3A. It can be also observed that the peak center shifts to smaller angles. The state can be suggested that the plane 0 0 4 of the graphite is due to the decrease in the number of layers. Indeed, other researchers have found similar diffraction patterns for this plane [29, 35].

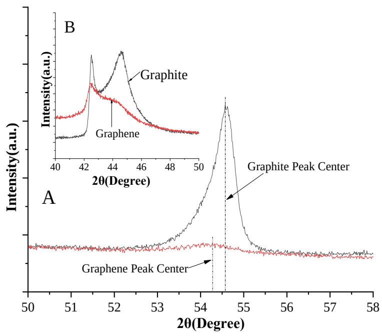

Figure 3. Graphite and graphene diffraction patterns in other planes A The pattern of peaks of the 1 0 0 and 1 0 1 planes B The pattern of peak of the 0 0 4 plane

3.2. Raman spectroscopy

Raman spectroscopy is a powerful method used to analyze the structure of crystalline materials. This technique is a non-destructive, fast and accurate technique estimated the defect density and the number and quality of graphene layers [29]. Carbon structures have 3 base peaks, named D peak (around 1350 cm^{-1}), G peak (around 1580 cm^{-1}) and 2D peak (around 2700cm^{-1}) [34]. The D peak shows the defects in the crystal structure, while the G band shows the vibrations of the carbon atoms between the layers and the crystallized structures. The 2D band is related to the stacking of the structure [39].

Raman spectra of the sample produced exfoliation method are shown in Figure 4. According to Figure 4B, the D band of graphite has a very low intensity at 1333 cm^{-1}, D' band at 1621cm^{-1} and the G band is a very strong peak at 1582 cm^{-1}. While the presence of the G peak signs the crystal structure of the graphite, the presence of the weak D peak indicates that the graphite contains partial defects in its structure [41]. D' peak is also related to the disorder of edge carbons [42, 43].

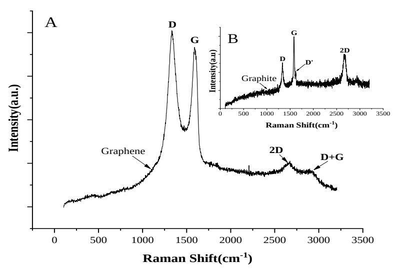

Figure 4. A Raman spectrum of graphene B Raman spectrum of graphite

The intense 2D peak at 2661 cm^{-1} originates from two-phonon double resonance**.** These similar results were also reported by other researchers [41, 42, 44]**.** After the exfoliation, the structure, D and G peaks are seen at 1330 cm^{-1} and 1594 cm^{-1} respectively (Figure 4A). Especially the increase in the density of the D peak is remarkable.

Table 2. Raman analysis of studied graphene samples

Sample	D Peak Position (cm^{-1}) Intensity (a.u.)	G Peak Position (cm^{-1}) Intensity (a.u.)	2D Peak Position (cm^{-1}) Intensity (a.u.)	I_D/ I_G	I_{2D}/ I_G
Graphite	1333 683	1582 994	2660 793	0,68	0.79
Graphene	1333 10007	1590 9200	2650 4010	1.08	0.44

It can be the result of an increase in defects in the crystal structure due to the oxygen-containing functional groups attached to the graphite layers during the exfoliation process [45]. The G peak can be seen to be over 1590cm^{-1}. Chamoli showed that this is an indicator of the standoff of oxygen functional groups from exfoliated nano sheets [46].

On the other hand, it is observed that the 2D peak of the exfoliated graphene is smaller and wider compared to the graphite [29, 34, 45, 47]. This result proves that the number of stacks and the number of layers is reduced**.** In addition that the result shows that transform from graphite to multilayer graphene [29, 41, 48]. Petrovski reported that 2D peak which is less pronounced and broad is indicated the asset of multilayered graphene (>8-layers) [29]. Ferrari explained that the broad 2D peak suggests the presence of multilayer graphene [41]. Beside that the D+G peak at 2910 cm^{-1} is related disorder of graphene structure [26, 34]. These results have also been reported in previous studies [41, 45, 47, 49].

According to Firdhouse, the shift of G peak around 20-30cm^{-1} indicates 5-20 graphene layer. Accordingly, the shift of the G peak in this study indicates the 5-20 layer number of the graphene layer [50-52]. This result is compatible with the number of layers obtained from the XRD results analysis. On the other hand, the I_D/I_G ratio gives information about the graphene quality while I_{2D}/I_G gives information about the number of layers of graphene [29, 53]**.**

I_D/I_G and I_{2D}/I_G ratios calculated using Figure 4 are given in Table 2. Accordingly, the I_D/I_G ratio of 1.25 shows that there are some defects in the graphene structure caused by the edge plane of the graphene sheets [41, 54]. This result has also been reported in previous studies [43, 53, 55]. The I_{2D}/I_G value of the exfoliated graphene is shown in Table 2. Gupta reported that when the number of graphene layers decreased, the value of I_{2D}/I_G increased. The relatively low I_{2D}/I_G ratio indicates mostly multilayer graphene [56].

Nguyen calculated the graphene I_{2D}/I_G ratio as 0.44 and reported that the graphene produced was multilayer [57]. Other researchers have obtained similar results.[53, 58]. According to the results, it has been understood that multilayer graphene was formed from graphite. Moreover, the crystallite size of graphene has calculated according to the Tuinstra and Koenig Equation 4 and 5:

$$\frac{I_D}{I_G} = \frac{C(\lambda)}{L_a} \quad (4)$$

$$L_a = C(\lambda)\frac{I_G}{I_D} \quad (5)$$

where the pre-factor C (λ) is equal to 4.95 for 532nm. The L_a value was calculated as 4.52 nm according to the equation. The result is compatible with the literature [29, 53]. In addition, there is a difference between the L_a value calculated from the Tuinstra and Koenig equation and the value calculated from the Debye Sheerer equation. The reason of the difference the result of the spectroscopy technique. While first technique is based on X-ray reflections, the other is based on changes in the Raman spectrum such as frequency shifts.

3.3. Fourier transform infrared spectroscopy

Infrared Spectroscopy (IR) provides a fast and reliable technique for identifying and characterizing the chemical structures of many substances, from biomaterials to composite materials, liquids and gases [59, 60]. F-TIR spectra of graphene nanosheets produced by exfoliation method are presented in Figure 5.

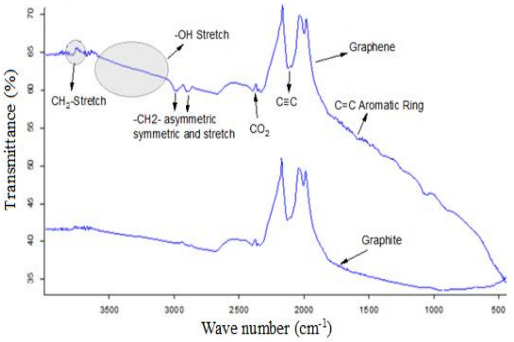

Figure 5. F-TIR spectra of graphite and graphene nanosheets

It can be seen that the vibrations of the functional groups are reasonably weak in the Figure 5. This shows that there are no functional groups in the nanosheets. It can be suggested that high heat generated during exfoliation leads to that. Due to the high temperature, the oxygen groups formed between the layers may be removed again. Therefore, the graphene nanosheets produced have a structure known in the literature as pristine graphene [61]. On the other hand, the F-TIR spectra of the graphene nano sheets synthesized is consistent with the literature [62-64]. Furthermore, in the F-TIR spectrum, the peak of CO_2 gas absorbed from the environment or formed between layers can be seen around 2350 cm^{-1}. In addition, the difference between graphene and graphite transmittance values is quite evident in figure 5. This may be interpreted as a decrease in the number of layers. F-TIR results also confirm the conversion from graphite to graphene nanosheets.

3.4. Scanning electron microscope

Scanning electron microscopy (SEM) is one of the best techniques used to study surface morphologies among modern image analysis methods.

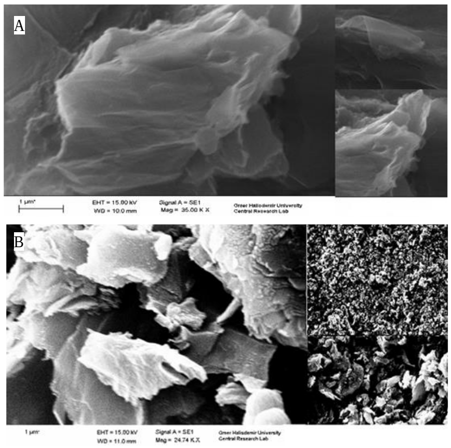

Figure 6. A- SEM images of graphene B- SEM images of graphite

SEM images of graphene and exfoliation graphite are shown in Figure 6. It can be seen that from Figure 6 while the graphite structure is shown a flat, thick structure consisting of layers, the structure of the exfoliation graphene is seen wrinkled and thin membrane-like structure [27-29, 38, 65]. This is due to the bending and buckling caused by the thermal stability of graphene during exfoliation. This may be regarded as an indication of the conversion from graphite to graphene as a result of an electrochemical process. The very thin and transparent structure (small picture) formed as a result of exfoliation confirms the previously calculated number of layers.

4. Conclusion

To produce graphene by electrochemical exfoliation technique, a graphite rod as a carbon source, a pencil tip as a cathode, and sulfuric acid as an electrolyte was used Multilayer graphene nanosheets were produced by this method. Morphological and thermal characteristic of graphene nanosheets were performed by XRD, Raman Spectroscopy, F-TIR Spectroscopy and SEM measurements. According to the XRD results, it was found that the graphene nano sheet structure is multi-layer (about 9-10 layers). The Raman Spectroscopy results shown that there are some structural defects in the graphene nanosheets. F-TIR results confirmed that the products are pristine graphene structures. SEM results showed that graphene layers were observed in thin layers. The results showed that low-cost multilayer graphene can be produced with the electrochemical exfoliation method.

The produced graphene can be used as a cathode material instead of the rather expensive pure platinum in the pen tip. The materials used in the experiment can be obtained from more cost-effective materials has further reduced the cost of the produced graphene. The electrochemical method is a very easy and useful method in graphene production. However, further investigation of the effect of changes in experimental inputs on graphene may provide the production of graphene with more controllable properties for future studies.

Article Information Form

Acknowledgments

We would like to thank the staff of Niğde University Central Research Laboratory

Funding

This work was funded by Niğde University Research Projects Unit under the grant no. FEB 2018/19.

The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the authors

Author Contributions

The authors declare their equal contribution to this publication. All authors have read and agreed to the published version of the manuscript.

The Declaration of Ethics Committee Approval

The author declares that this document does not require an ethics committee approval or any special permission.

The Declaration of Research and Publication Ethics

The author of the paper declares that he complies with the scientific, ethical, and quotation rules of SAUJS in all processes of the paper and that he does not make any falsification on the data collected. In addition, he declares that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

References

[1] A. K. Geim,K. S. Novoselov, "The rise of graphene", Nature Mater, 6, p. 183-191, 2007

[2] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva,A. A. Firsov, "Electric field effect in atomically thin carbon films", Science, 306, p. 666-669, 2004

[3] K. S. Novoselov, A. K. Geim, S. Morozov, D. Jiang, M. I. Katsnelson, I. Grigorieva, S. Dubonos, Firsov, A A, "Two-dimensional gas of massless Dirac fermions in graphene", Nature, 438, p. 197, 2005

[4] Y. Zhang, Y.-W. Tan, H. L. Stormer,P. Kim, "Experimental observation of the quantum Hall effect and Berry's phase in graphene", Nature, 438, p. 201, 2005

[5] C. Lee, X. Wei, J. W. Kysar, J. Hone, "Measurement of the elastic properties and intrinsic strength of monolayer graphene", Science, 321, p. 385-388, 2008

[6] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao,C. N. Lau, "Superior thermal conductivity of single-layer graphene", Nano Letters, 8, p. 902-907, 2008

[7] K. I. Bolotin, K. J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, H. Stormer, "Ultrahigh electron mobility in suspended graphene", Solid State Communications, 146, p. 351-355, 2008

[8] A. A. Balandin, "Thermal properties of graphene and nanostructured carbon materials", Nature Materials, 10, p. 569, 2011

[9] V. B. Mohan, K.-t. Lau, D. Hui, D. Bhattacharyya, "Graphene-based materials and their composites: a review on production, applications and product limitations", Composites Part B: Engineering, 142, p. 200-220, 2018

[10] J. Lu, J.-x. Yang, J. Wang, A. Lim, S. Wang,K. P. Loh, "One-pot synthesis of fluorescent carbon nanoribbons, nanoparticles, and graphene by the exfoliation of graphite in ionic liquids", ACS Nano, 3, p. 2367-2375, 2009

[11] H. B. Heersche, P. Jarillo-Herrero, J. B. Oostinga, L. M. Vandersypen,A. F. Morpurgo, "Bipolar supercurrent in graphene", Nature, 446, p. 56, 2007

[12] L. Vicarelli, M. Vitiello, D. Coquillat, A. Lombardo, A. C. Ferrari, W. Knap, M. Polini, V. Pellegrini,A. Tredicucci, "Graphene field-effect transistors as room-temperature terahertz detectors", Nature Materials, 11, p. 865, 2012

[13] M. D. Mukherjee, C. Dhand, N. Dwivedi, B. P. Singh, G. Sumana, V. V. Agarwal, J. S. Tawale, B. D. Malhotra, "Facile synthesis of 2-dimensional transparent graphene flakes for nucleic acid detection", Sensors and Actuators B: Chemical, 210, p. 281-289, 2015

[14] S. J. Wang, Y. Geng, Q. Zheng,J.-K. Kim, "Fabrication of highly conducting and transparent graphene films", Carbon, 48, p. 1815-1823, 2010

[15] X. Song, Z. Shi, X. Tan, S. Zhang, G. Liu,K. Wu, "One-step solvent exfoliation of graphite to produce a highly-sensitive electrochemical sensor for tartrazine", Sensors and Actuators B: Chemical, 197, p. 104-108, 2014

[16] S. Kim, H. S. Lee, J. M. Kim, S. W. Seo, J. H. Kim, C. W. Jang,S.-H. Choi, "Effect of layer number on flexible perovskite solar cells employing multiple layers of graphene as transparent conductive electrodes", Journal of Alloys and Compounds, 744, p. 404-411, 2018

[17] K. Parvez, R. Li, S. R. Puniredd, Y. Hernandez, F. Hinkel, S. Wang, X. Feng, K. Müllen, "Electrochemically exfoliated graphene as solution-processable, highly conductive electrodes for organic electronics", ACS Nano, 7, p. 3598-3606, 2013

[18] Z. Y. Xia, G. Giambastiani, C. Christodoulou, M. V. Nardi, N. Koch, E. Treossi, V. Bellani, S. Pezzini, F. Corticelli,V. Morandi, "Synergic exfoliation of graphene with organic molecules and inorganic ions for the electrochemical production of flexible electrodes", ChemPlusChem, 79, p. 439-446, 2014

[19] Y. L. Zhong, Z. Tian, G. P. Simon, D. Li, "Scalable production of graphene via wet chemistry: progress and challenges", Materials Today, 18, p. 73-78, 2015

[20] Z. Chen, W. Ren, L. Gao, B. Liu, S. Pei, H. - M. Cheng, "Three-dimensional flexible and conductive interconnected graphene networks grown by chemical vapour deposition", Nature Materials, 10, p. 424, 2011

[21] R. Singh,C. C. Tripathi, "Synthesis of Colloidal Graphene by Electrochemical Exfoliation of Graphite in Lithium Sulphate", Materials Today: Proceedings, 5, p. 973-979, 2018

[22] J. Chen, B. Yao, C. Li, G. Shi, "An improved Hummers method for eco-friendly synthesis of graphene oxide", Carbon, 64, p. 225-229, 2013

[23] Z. Yang, S. Xu, L. Zhao, J. Zhang, Z. Wang, X. Chen, X. Cheng, F. Yu, X. Zhao, "A new direct growth method of graphene on Si-face of 6H-SiC by synergy of the inner and external carbon sources", Applied Surface Science, 436, p. 511-518, 2018

[24] A. T. Najafabadi,E. Gyenge, "High-yield graphene production by electrochemical exfoliation of graphite: Novel ionic liquid (IL)–acetonitrile electrolyte with low IL content", Carbon, 71, p. 58-69, 2014

[25] T. Güzel, "Investigation of the usability of nitric acid electrolyte in graphene production by electrochemical method", Fullerenes, Nanotubes and Carbon Nanostructures, 1-8, 2020

[26] R. I. Jibrael, M. K. Mohammed, "Production of graphene powder by electrochemical exfoliation of graphite electrodes immersed in aqueous solution", Optik, 127, p. 6384-6389, 2016

[27] S. Yang, S. Brüller, Z.-S. Wu, Z. Liu, K. Parvez, R. Dong, F. Richard, P. Samorì, X. Feng, K. Müllen, "Organic radical-assisted electrochemical exfoliation for the scalable production of high-quality graphene", Journal of the American Chemical Society, 137, p. 13927-13932, 2015

[28] M. Coroş, F. Pogăcean, M.-C. Roşu, C. Socaci, G. Borodi, L. Mageruşan, A. R. Biriş,S. Pruneanu, "Simple and cost-effective synthesis of graphene by electrochemical exfoliation of graphite rods", RSC Advances, 6, p. 2651-2661, 2016

[29] A. Petrovski, A. T. Dimitrov, A. Grozdanov, P. Paunović, B. Andonović, G. Gentile, M. Avella,B. Ranguelov, "Study of Graphene Obtained by Electrolysis in Sulfuric Acid Electrolytes", SciFed Nanotech Research Letters, 2017

[30] G. Wang, B. Wang, J. Park, Y. Wang, B. Sun,J. Yao, "Highly efficient and large-scale synthesis of graphene by electrolytic exfoliation", Carbon, 47, p. 3242-3246, 2009

[31] J. Munuera, J. Paredes, S. Villar-Rodil, A. Martínez-Alonso,J. Tascón, "A simple strategy to improve the yield of graphene nanosheets in the anodic exfoliation of graphite foil", Carbon, 115, p. 625-628, 2017

[32] Q. Zhou, Y. Lu, H. Xu, "High-yield production of high-quality graphene by novel electrochemical exfoliation at air-electrolyte interface", Materials Letters, 235, p. 153-156, 2019

[33] K. Chen,D. Xue, "From graphite-clay composites to graphene electrode materials: in-situ electrochemical oxidation and functionalization", Materials Research Bulletin, 96, p. 281-285, 2017

[34] M. Alanyalıoğlu, J. J. Segura, J. Oró-Solè,N. Casañ-Pastor, "The synthesis of graphene sheets with controlled thickness and order using surfactant-assisted electrochemical processes", Carbon, 50, p. 142-152, 2012

[35] K. Chen,D. Xue, "Preparation of colloidal graphene in quantity by electrochemical exfoliation", Journal of Colloid and Interface Science, 436, p. 41-46, 2014

[36] S. K. Sahoo, A. Mallik, "Simple, fast and cost-effective electrochemical synthesis of few layer graphene nanosheets", Nano, 10, p. 1550019, 2015

[37] I. Afanasov, O. Shornikova, D. Kirilenko, I. Vlasov, L. Zhang, J. Verbeeck, V. Avdeev,G. Van Tendeloo, "Graphite structural transformations during intercalation by HNO3 and exfoliation", Carbon, 48, p. 1862-1865, 2010

[38] K. Chen, D. Xue, S. Komarneni, "Nanoclay assisted electrochemical exfoliation of pencil core to high conductive graphene thin-film electrode", Journal of Colloid and Interface Science, 487, p. 156-161, 2017

[39] F. T. Johra, J.-W. Lee,W.-G. Jung, "Facile and safe graphene preparation on solution based platform", Journal of Industrial and Engineering Chemistry, 20, p. 2883-2887, 2014

[40] B. E. Warren, *X-ray Diffraction*. 1990: Courier Corporation.

[41] A. C. Ferrari, J. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. Novoselov,S. Roth, "Raman spectrum of graphene and graphene layers", Physical Review Letters, 97, p. 187401, 2006

[42] K. S. Rao, J. Senthilnathan, Y.-F. Liu,M. Yoshimura, "Role of peroxide ions in formation of graphene nanosheets by electrochemical exfoliation of graphite", Scientific Reports, 4, p. 4237, 2014

[43] A. Radoń, P. Włodarczyk,D. Łukowiec, "Structure, temperature and frequency dependent electrical conductivity of oxidized and reduced electrochemically exfoliated graphite", Physica E: Low-dimensional Systems and Nanostructures, 99, p. 82-90, 2018

[44] M. Pimenta, G. Dresselhaus, M. S. Dresselhaus, L. Cancado, A. Jorio,R. Saito, "Studying disorder in graphite-based systems by Raman spectroscopy", Physical Chemistry Chemical Physics, 9, p. 1276-1290, 2007

[45] R. Singh,C. C. Tripathi, "Electrochemical exfoliation of graphite into graphene for flexible supercapacitor application", Materials Today: Proceedings, 5, p. 1125-1130, 2018

[46] P. Chamoli, M. K. Das, K. K. Kar, "Green synthesis of less defect density bilayer graphene", Graphene, 3, p. 56-60, 2015

[47] S.-H. Lee, S.-D. Seo, K.-S. Park, H.-W. Shim,D.-W. Kim, "Synthesis of graphene nanosheets by the electrolytic exfoliation of graphite and their direct assembly for lithium ion battery anodes", Materials Chemistry and Physics, 135, p. 309-316, 2012

[48] L. Malard, M. Pimenta, G. Dresselhaus, M. Dresselhaus, "Raman spectroscopy in graphene", Physics Reports, 473, p. 51-87, 2009

[49] C.-Y. Su, A.-Y. Lu, Y. Xu, F.-R. Chen, A. N. Khlobystov, L.-J. Li, "High-quality thin graphene films from fast electrochemical exfoliation", ACS Nano, 5, p. 2332-2339, 2011

[50] M. J. Firdhouse, P. Lalitha, "Eco-friendly synthesis of graphene using the aqueous extract of Amaranthus dubius", Carbon:Science and Technology, 5, p. 253-259, 2013

[51] V. Singh, D. Joung, L. Zhai, S. Das, S. I. Khondaker,S. Seal, "Graphene based materials: past, present and future", Progress in Materials Science, 56, p. 1178-1271, 2011

[52] V. Chabot, B. Kim, B. Sloper, C. Tzoganakis,A. Yu, "High yield production and purification of few layer graphene by Gum Arabic assisted physical sonication", Scientific Reports, 3, p. 1378, 2013

[53] H. S. Wahab, S. H. Ali,A. A. Hussein, "Synthesis and characterization of graphene by Raman spectroscopy", Journal of Materials Sciences and Applications, 1, p. 130-135, 2015

[54] R. Navik, Y. Gai, W. Wang,Y. Zhao, "Curcumin-assisted ultrasound exfoliation of graphite to graphene in ethanol", Ultrasonics Sonochemistry, 48, p. 96-102, 2018

[55] A. Ambrosi, M. Pumera, "Electrochemically exfoliated graphene and graphene oxide for energy storage and electrochemistry applications", Chemistry–A European Journal, 22, p. 153-159, 2016

[56] A. Gupta, G. Chen, P. Joshi, S. Tadigadapa,P. Eklund, "Raman scattering from high-frequency phonons in supported n-graphene layer films", Nano Letters, 6, p. 2667-2673, 2006

[57] H. D. Le, T. T. T. Ngo, D. Q. Le, X. N. Nguyen,N. M. Phan, "Synthesis of multi-layer graphene films on copper tape by atmospheric pressure chemical vapor deposition method", Advances in Natural Sciences: Nanoscience and Nanotechnology, 4, p. 035012, 2013

[58] A. Hamra, H. Lim, W. Chee,N. Huang, "Electro-exfoliating graphene from graphite for direct fabrication of supercapacitor", Applied Surface Science, 360, p. 213-223, 2016

[59] Y.-H. Son, W.-C. Jung, J.-I. Jeong, N.-G. Park, I.-S. Kim,I.-H. Bae, "FTIR characteristics of hydrogenated amorphous carbon films prepared by Ecr-Pecvd", Journal-Korean Physical Society, 39, p. 713-717, 2001

[60] E. Vaghri, Z. Khalaj,M. Ghoranneviss, "Preparation and characterization of diamond-like carbon films on various substrates by PECVD system", Studia Univ Babes-Bolyai Chemia, 57, p. 143-150, 2012

[61] M. Hayyan, A. Abo-Hamad, M. A. AlSaadi,M. A. Hashim, "Functionalization of graphene using deep eutectic solvents", Nanoscale Research Letters, 10, p. 324, 2015

[62] A. Mir, A. Shukla, "Bilayer-rich graphene suspension from electrochemical exfoliation of graphite", Materials & Design, 156, p. 62-70, 2018

[63] O. Sadak, A. K. Sundramoorthy,S. Gunasekaran, "Facile and green synthesis of highly conductive graphene paper", Carbon, 138, p. 108-117, 2018

[64] Z. M. Marković, B. M. Babić, M. Dramićanin, I. H. Antunović, V. B. Pavlović, D. Peruško,B. T. Marković, "Preparation of highly conductive carbon cryogel based on pristine graphene", Synthetic Metals, 162, p. 743-747, 2012

[65] F. Tavakoli, M. Salavati-Niasari,F. Mohandes, "Green synthesis and characterization of graphene nanosheets", Materials Research Bulletin, 63, p. 51-57, 2015