doi:10.55385/kastamonujes.1477345 KUJES 10(1):38-43, 2024

Kastamonu University
Journal of Engineering and Sciences
e-ISSN 2667-8209
http://dergipark.gov.tr/kastamonujes

Reduced Graphene Synthesis via Eco-Friendly Electrochemical Exfoliation Method

Gülbahar Bilgiç Tüzemen

Department of Metallurgy and Material Engineering, Faculty of Engineering-Architecture, Nevşehir Hacı Bektaş Veli University, Nevşehir, Türkiye
Corresponding Author: glbhrblg@nevsehir.edu.tr

Received: **May 2, 2024** ◆ Accepted: **June 14, 2024** ◆ Published Online: **June 28, 2024**

Abstract: A novel approach to mass producing graphene without inadvertent damage was needed to meet the increasing demand for the material. Graphite electrochemical exfoliation (EE) is an intriguing method for the large-scale, quick, and easy manufacture of graphene. Using leftover whey as an electrolyte, the EE of commercial graphite was examined in this work. It was shown that a straightforward and affordable exfoliation technique may produce graphene that, in the absence of functionalization or surfactant, forms a stable dispersion in the waste solvent. Because wastewater is acidic, it has been shown that storing it at +4 degrees aids EE. X-ray diffraction (XRD) was used to satisfactorily validate the manufactured graphene's existence. The results point to a low-cost method of producing graphene and graphene oxide.

Keywords: Graphene, waste cheese water, electrochemical exfoliation

Öz: Grafene yönelik artan talep, gereksiz hasara yol açmadan seri üretime geçmenin yeni bir yolunu gerektiriyordu. Bu yüzden grafitin pul pul dökülmesi basit, hızlı ve büyük ölçekli grafen üretimi için ilginç bir yaklaşımdır. Bu çalışmada atık peynir altı suyu elektrolit olarak kullanılarak ticari grafitin elektrokimysal pul pul dökülmesi araştırıldı. İşlevselleştirme ve yüzey aktif madde olmadan atık çözücü içinde stabil bir dağılım oluşturan grafen hazırlamak için basit ve uygun maliyetli bir elektrokimysal pul pul dökülme yöntemi gösterilmiştir. +4 derecede depolanan atık suyun asidik yapısından dolayı elektrokimyasal pul pul dökülmeye yardımcı olduğu gözlemlenmiştir. Üretilen grafenin varlığı X-ışını kırınımı (XRD) ile başarıyla doğrulandı. Bulgular, grafen ve grafen oksidin sentezlenmesi için düşük maliyetli bir üretim süreci önermektedir.

Anahtar Kelimeler: Grafen, atık peynir suyu, elektrokimyasal pul pul dökülme

1. Introduction

Graphene is a planar sheet one atom thick, composed of hexagon-shaped carbon atoms from sp^2 hybridization. Its mechanical, thermal, optical, and electrical qualities are outstanding. Moreover, graphene acts as a semimetal and has a zero-band gap due to its two-dimensional structure [1]. Graphene may be produced by several methods, such as ultrahigh vacuum annealing of single crystal SiC, mechanical or electrochemical exfoliation and cleavage, and chemical vapor deposition [2-4]. A low-cost, environmentally friendly technique for producing high-yield graphene is EE of graphite, which yields one-atom-thick graphene with desired features. It has long been recognized that graphite and other species may combine to make helpful intercalation compounds, or graphite intercalation compounds, which are frequently created electrochemically. Researchers have expanded GIC chemistry to electrochemically exfoliate graphene from natural graphite in light of the recent discovery of graphene [2, 3]. One of the increasing number of methods for producing graphene is electrochemical exfoliation. Wet chemical exfoliation techniques, like the modified Hummers process used to make graphene oxide, are connected to the electrochemical approach. However, unlike conventional techniques, which frequently rely on strong oxidants, electrochemical techniques use the conductive qualities of graphite to intercalate molecules between graphene layers. Much work has been done recently on the easy, quick, affordable, and environmentally acceptable EE of graphite to produce high-grade graphene [5]. Comparing this procedure to other conventional methods, it appears promising for manufacturing huge amounts of graphene [2]. Moreover, functionalized graphene might be produced by the exfoliation process. During the procedure, some factors need to be controlled, including the number of probes, the amount of current utilized, and the chemicals employed. The methods are similar in that an electrolyte (aqueous or nonaqueous solution, for example) and an electric current are often used to induce structural expansion in a graphite electrode [2]. Depending on the charge of the intermediate ions, the graphite electrode can operate as an anode or cathode and exhibit oxidation or reduction processes, respectively.

A positive or negative charge can be applied to the material by employing graphite as an electrode, which promotes the intercalation of oppositely charged ions and facilitates exfoliation. The electrochemical process is promising for

producing graphene in large quantities and may offer several benefits over conventional chemical approaches [5]. An example of a wet chemical procedure that can be less expensive for mass manufacturing is the electrochemical approach, which is similar to mechanical exfoliation, molecular assembly, and chemical vapor deposition (CVD). Even more than this, by using electrochemical activation instead of harsh chemicals, electrochemical manufacturing may be able to achieve a simpler stage in the purification of the final product. Electrochemically generated graphene can have a controllable degree of oxidation and low-hole flaws, making it a reasonably high-quality material. Electrochemically produced graphene is expected to have industrial uses in energy storage, electronics, coatings, and nanocomposites in other words, it will be used in all of the applications that have been proposed for graphene [5-14]. Although many methods have been proposed as successful in generating graphene, no one has yet discovered a flawless method that produces graphene without any flaws. As previously mentioned, compared to other methods, EE is a simple, rapid, and inexpensive process to produce graphene. Enough high-quality graphene materials need to be developed to satisfy the requirements of all these technological applications. During the EE process, when direct current is applied to two electrode arrays, strong particles are formed at both electrodes, and the anodic graphite and electrolyte begin to separate [6]. Unlike other peeling techniques, this approach requires no equipment and usually requires natural light. Furthermore, it is less harmful than other chemical methods that include potentially hazardous solvents or reagents [6, 7].

A straightforward and efficient method for producing graphene involves electrochemically exfoliating graphite rods in acidic liquids, as suggested by Coroş, M. and associates [11]. The graphene oxide peak diminishes or even vanishes when the EE trend is reduced from +6 to +2.5 V, according to the nanosheets' XRD patterns. It has been shown that by varying the applied voltage, graphene with varying degrees of oxidation may be generated. At a bias of +3 V, an ideal graphene sample was made in an H_2SO_4:HNO_3 combination.

The simple synthesis of graphene by electro-exfoliation employing several oxidizing agents (HNO_3, $NaNO_3$, H_2SO_4, and H_2O_2) in the presence of sodium dodecyl benzenesulfonate as a surfactant was proven by A.A.B. Hamra and colleagues [12]. The EE of graphite rods was dramatically altered by several surfactant-oxidizing agent solutions at varied concentrations. Moreover, graphene is directly generated via vacuum filtration and used as a supercapacitor electrode. The impact of electrolyte type on capacitance performance was examined using nylon membrane and polymer gel, both of which contained 2.0 M potassium hydroxide. The polymer gel electrolyte demonstrated an astounding capacity retention rate of more than 100% after 1000 charge/discharge cycles, whereas the nylon membrane electrolyte recorded a capacity retention rate of just 94%. The manufactured supercapacitor's capacity to light a light-emitting diode while charging reveals its promise for practical uses.

The EE of two distinct graphite predecessors at an applied direct current voltage of +12 V was shown by Marković et al [13]. The results of the characterization methods (X-ray diffraction, X-photoelectron spectroscopy, etc.) indicated that the exfoliated powder is highly functionalized and resembles graphene oxide in terms of its low carbon/oxygen concentration. After being disseminated in N,N′-dimethylformamide, the exfoliated graphene sheets were vacuum-filtered onto ano-discs and then moved to glass-ceramic substrates.

Here, a very effective method for processing graphene from graphite using electrolytic exfoliation for mass production is presented. In addition, by using waste whey as an electrolyte in the study, the cost was reduced, and the presence of harmful chemicals was reduced. A simple and cost-effective exfoliation method has been demonstrated to prepare graphene forming a stable dispersion in the waste solvent, without any functionalization and surfactant. It has been observed that wastewater stored at +4 degrees helps EE due to its acidic nature. The existence of the produced graphene was successfully confirmed by XRD. The findings suggest a low-cost production process for synthesizing graphene and graphene oxide.

2. Material and Method

Materials and characterization

Two graphite rods with a diameter of 5.6 mm. Sodium sulphate Na_2SO_4 were supplied by Merck assay and used as electrolytes. All of the synthesis procedures involved the use of distilled water. The two electrodes received a DC voltage of 10 V as a constant potential (NEL Electronic). XRD measurements were performed on a Rigaku diffractometer X-ray Miniflex 600 model to identify the crystallographic structure of the graphene.

Graphene synthesis by electrochemical exfoliation

Figure 1 shows a schematic illustration of graphite EE. All experiments were carried out under ambient conditions. In this work, graphene was electrochemically synthesized using a traditional two-graphite rod electrode setup [14]. The wastewater whey to be used as the electrolyte in the experiment was filtered with qualitative filter paper to separate it from sediments. A graphite rod served as the working electrode and a second graphite rod served as the counter electrode for the EE. At a distance of around 2 cm, the anode and cathode graphite rods were positioned parallel to one another. A 100 ml solution of waste cheese water (+4 °C) and 10 g Na_2SO_4 (v/v) were used as the electrolyte. For one hour, the direct current (DC) bias voltage was maintained at 10 V. After the exfoliation process, 1 hour, the experimental setup was

turned off. The liquid part of the resulting graphene solution was poured, and the filtrate was centrifuged with distilled water at 1500 rpm for 5 minutes at room temperature three times. Following drying at 100 °C in a vacuum oven, the powder was produced [15]. During the entire electrochemical process, the release of gas bubbles was observed, which became denser with increasing electrolyte concentration. Figure 2 shows photographs of wastewater and the experimental setup.

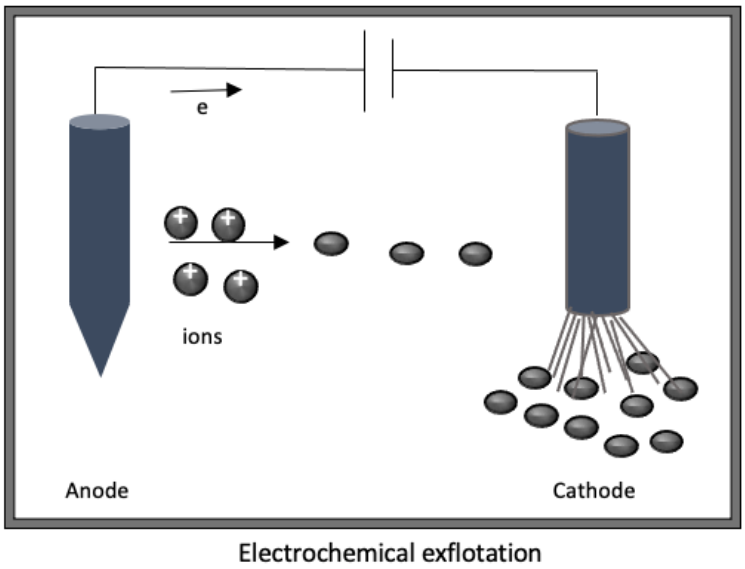

Figure 1. Diagram showing the equipment used in the electrolytic exfoliation method to synthesize graphene

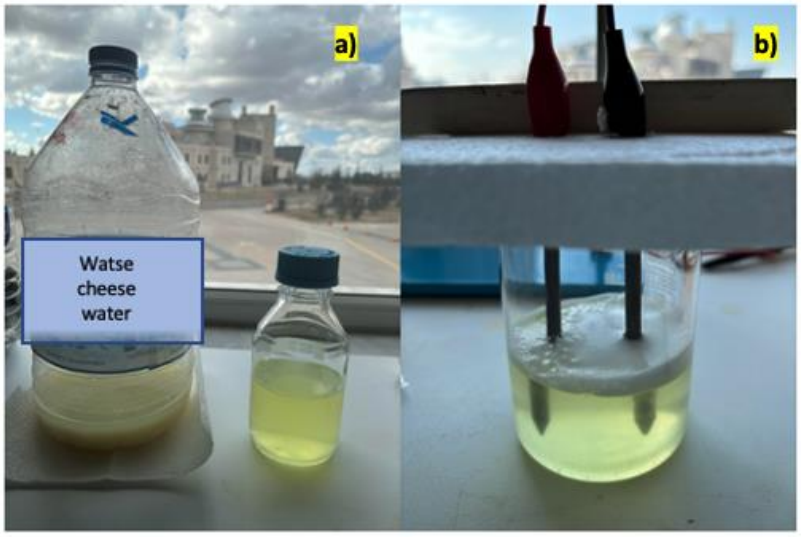

Figure 2. Photographs of (a) waste cheese water and (b) experimental setup

3. Result

The anode and cathode were separated by 2 cm and submerged in electrolyte to a depth of 100 mm prior to the electrical power being turned on [1]. Throughout the preparation process, it was noted that the electric current fluctuated but the voltage remained steady at 10 V. After electrolysis, a stable graphene dispersion was produced. To get bulk graphene particles, this supernatant was rinsed with DI water and then dried in a vacuum oven. Then, powder graphenes were analyzed by taking 5 g samples. Figure 3 shows the images of the anode and cathode electrodes before and after the electrolytic exfoliation reaction. It is clearly seen that the working area is corroded after the electrolytic exfoliation reaction of the graphite cathode electrode. Figure 4 images of the dispersion in the cell after the electrolytic exfoliation reaction (b) of the graphene dispersion after centrifugation are shown. Gas evolution was observed in the two-electrode cell. The graphene shed during the reaction accumulated at the bottom of the cell. After centrifugation, the graphene dispersion was overdried at 100 °C overnight to remove water.

Figure 3. Image of (a) anode and cathode electrodes before and (b) cathode electrodes after electrolytic exfoliation reaction

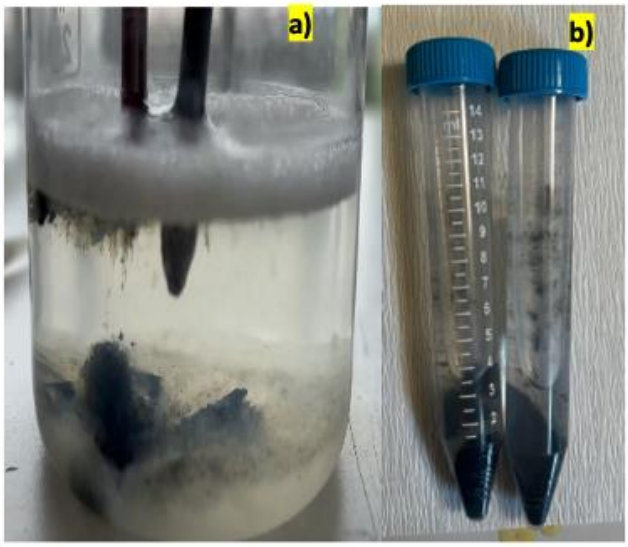

Figure 4. Photographs of (a) the graphene dispersion obtained by electrolytic exfoliation of graphite, (b) the state of the graphene dispersion after centrifugation

XRD was used to determine the exfoliated graphene's crystal structure and interlayer spacing. Three strong peaks at around 26.488°, 42°, and 54.5433°, which correspond to the (0 0 2), (1 0 1), and (0 0 4) crystallographic planes, respectively, are shown in Figure 5, which depicts the purification of the raw graphite powder [6]. The peak at $2\theta = 26°$, which corresponds to the (0 0 2) reflection of the graphitic structure and indicates the existence of graphene, is a hallmark interlayer stacking peak of aromatic systems [6, 12]. The XRD results, which are consistent with earlier research, demonstrated that graphite may be successfully exfoliated to produce graphene [12]. Figure 6 shows a Short Circuit Current versus time graph. In Figure 6 it can be seen that the current was at 0.36 when the experiment started. Meanwhile, the electrons released from the graphite anode began to move towards the cathode. After 5 minutes, this value reached the maximum value of 0.42. After 30 minutes, the current started to decrease and after an hour it dropped to 0.18.

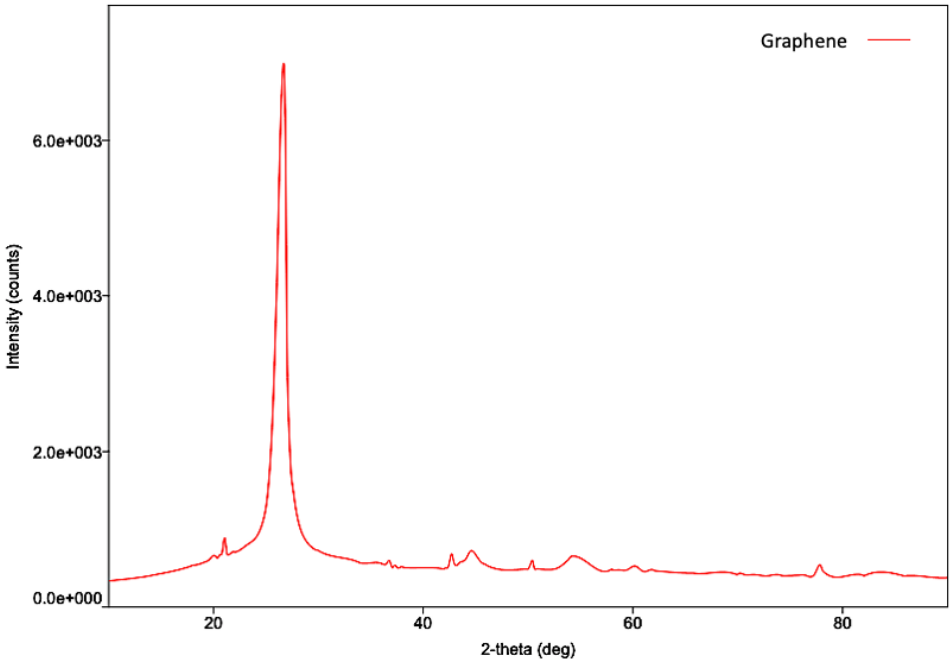

Figure 5. XRD spectrum of graphene

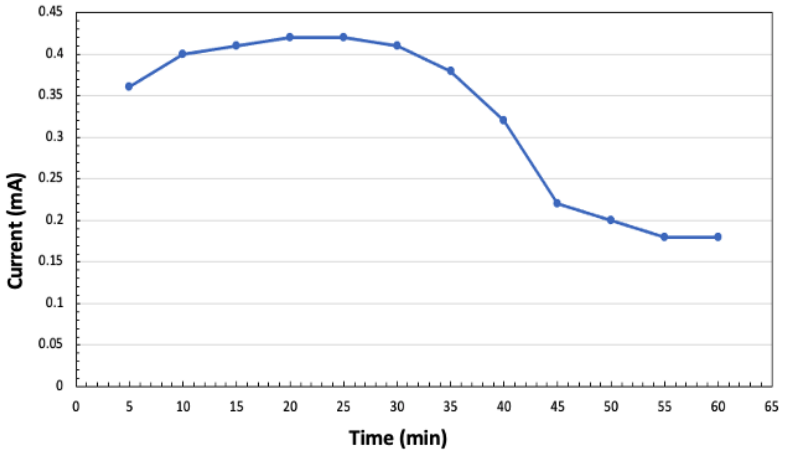

Figure 6. Current versus time graph

4. Discussion and Conclusion

In this work, leftover whey was used as the electrolyte in an extremely straightforward and inexpensive approach devised by EE to synthesize graphene from graphite rod. The exfoliation process was initiated by the wastewater weakening the bonding and interlayer forces inside the graphite during the effective reaction that occurred in the electrochemical cell. Graphene production was successfully achieved by 1-hour EE using a two-electrode arrangement at +10 V constant potential. Produced graphene can be used in various applications, especially energy applications. However, more experiments and characterizations are needed, and the electrolyte solution needs to be improved to achieve a more efficient reaction. Additionally, the study performed with two electrodes can be compared with a three-electrode cell. Thus, the usability of the graphene produced for supercapacitors and batteries can be discussed.

Conflict of Interest

All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

Ethics Committee Approval

Ethics committee approval is not required.

Author Contribution

Conceptization, methodology, laboratory analyzes, writing draft, proof reading and editing: GBT.

Acknowledgements

The author thank the editors and reviewers for their critical remarks and suggestions during the preparation of the manuscript.

5. References

[1] Sun, H., Xu, G., Lian, W., Kastiukas, G., Zhang, J., Zhang, X., Liu, W., Xing, F., & Ren, J. (2022). Electrochemical synthesis and property characterisation of graphene oxide using water as electrolyte. *Chemical Physics Letters*, *786*, 139206.

[2] Yu, P., Lowe, S. E., Simon, G. P., & Zhong, Y. L. (2015). Electrochemical exfoliation of graphite and production of functional graphene. *Current Opinion in Colloid & Interface Science*, *20*(5–6), 329–338.

[3] Liu, F., Wang, C., Sui, X., Riaz, M. A., Xu, M., Wei, L., & Chen, Y. (2019). Synthesis of graphene materials by electrochemical exfoliation: Recent progress and future potential. *Carbon Energy*, *1*(2), 173–199.

[4] Singh, R. (2021). Recent progress in the electrochemical exfoliation of colloidal graphene: A Review. *Colloids - Types, Preparation and Applications*.

[5] Shabbir, M. K., Akhtar, J., Thebo, K. H., & Kazi, M. (2024). Synthesis of highly efficient ternary phase graphene/bi/SNO2 photocatalyst for degradation of organic dye pollutants. *Optik*, *304*, 171734.

[6] Htwe, Y. Z. N., Chow, W. S., Suda, Y., Thant, A. A., & Mariatti, M. (2019). Effect of electrolytes and sonication times on the formation of graphene using an electrochemical exfoliation process. *Applied Surface Science*, *469*, 951–961.

[7] Coroş, M., Pogăcean, F., Roşu, M.-C., Socaci, C., Borodi, G., Mageruşan, L., Biriş, A. R., & Pruneanu, S. (2016). Simple and cost-effective synthesis of graphene by electrochemical exfoliation of graphite rods. *RSC Advances*, *6*(4), 2651–2661.

[8] Wang, G., Wang, B., Park, J., Wang, Y., Sun, B., & Yao, J. (2009). Highly efficient and large-scale synthesis of graphene by electrolytic exfoliation. *Carbon*, *47*(14), 3242–3246.

[9] Yang, S., Brüller, S., Wu, Z.-S., Liu, Z., Parvez, K., Dong, R., Richard, F., Samorì, P., Feng, X., & Müllen, K. (2015). Organic radical-assisted electrochemical exfoliation for the scalable production of high-quality graphene. *Journal of the American Chemical Society*, *137*(43), 13927–13932.

[10] Yang, Y., Wang, Z., & Zheng, S. (2021). Secondary exfoliation of electrolytic graphene oxide by ultrasound assisted microwave technique. *Nanomaterials*, *12*(1), 68.

[11] Coroş, M., Pogăcean, F., Măgeruşan, L., Roşu, M.-C., Porav, A. S., Socaci, C., Bende, A., Stefan-van Staden, R.-I., & Pruneanu, S. (2018). Graphene-porphyrin composite synthesis through graphite exfoliation: The electrochemical sensing of Catechol. *Sensors and Actuators B: Chemical*, *256*, 665–673.

[12] Hamra, A. A. B., Lim, H. N., Chee, W. K., & Huang, N. M. (2016). Electro-exfoliating graphene from graphite for direct fabrication of Supercapacitor. *Applied Surface Science*, *360*, 213–223.

[13] Marković, Z. M., Budimir, M. D., Kepić, D. P., Holclajtner-Antunović, I. D., Marinović-Cincović, M. T., Dramićanin, M. D., Spasojević, V. D., Peruško, D. B., Špitalský, Z., Mičušik, M., Pavlović, V. B., & Todorović-Marković, B. M. (2016). Semi-transparent, conductive thin films of electrochemical exfoliated graphene. *RSC Advances*, *6*(45), 39275–39283.

[14] Fang, S., Lin, Y., & Hu, Y. H. (2019). Recent advances in green, safe, and fast production of graphene oxide via electrochemical approaches. *ACS Sustainable Chemistry & Engineering*, *7*(15), 12671–12681.

[15] Su, C.-Y., Lu, A.-Y., Xu, Y., Chen, F.-R., Khlobystov, A. N., & Li, L.-J. (2011). High-quality thin graphene films from fast electrochemical exfoliation. *ACS Nano*, *5*(3), 2332–2339.