

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,800

Open access books available

122,000

International authors and editors

135M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Ultrasonic-Assisted Cathodic Plasma Electrolysis Approach for Producing of Graphene Nanosheets

Nguyen Van Truong, Nguyen Quoc Dung, Nguyen Nhat Huy, Pham Van Hao and Dang Van Thanh

Abstract

In this chapter, we review on the production of graphene by ultrasonic-assisted cathodic plasma electrolysis approach which involves a combination process of conventional electrolysis and plasma at ambient pressure and moderate temperature. Firstly, we review on the techniques for electrochemical preparation of graphene. Then, we briefly describe plasma electrolysis approach for producing of graphene. The mechanism, advantages, and disadvantages of this technique are discussed in detail.

Keywords: ultrasonic assisted, graphene nanosheets, cathodic electrochemical discharge, plasma, electrolysis

1. Introduction

Over the past decades, graphene is one of the hottest topics in many research fields. Up to date, a numerous of possible technological applications using graphene has been explored for energy, storage, optoelectronics, energy conversion, solar cell, flexible devices, and photonics [1–3]. Graphene is currently prepared by two typical top-down and bottom-up approaches with their advantages and drawbacks. For instance, chemical vapor deposition, classified as a chemical method, is an outstanding method because graphene can be obtained with high quality. However, it needs specific substrates, high temperature and vacuum, and limited transfer requirement while producing fewer quantities due to the slow process [4]. In terms of top-down technique, the most commonly used Hummer's method for graphite chemical exfoliation requires concentrated acids and strong oxidants for pretreating and is then followed by a sonication step [5]. Unfortunately, this method has a key bottleneck such as graphene structure containing many defects or functional groups, being time-consuming, and harsh oxidation condition. Furthermore, electrochemical exfoliation is emergently proven to be promising as a sustainable and green method for large-scale graphene production since it provides a single step and is user-friendly at moderate conditions [6].

Sonoelectrochemistry, an introduction of ultrasonic irradiation into electrochemical method, has become a potential approach for synthesizing nanomaterials owing to its simple step and being environmentally friendly [7]. Fundamentally, the

generation of cavitation bubbles is initiated by the propagation of pressure waves in a fluid [8, 9], and the collapse of cavitation bubbles is rapidly happening ($< \mu\text{s}$) to create local “hot spots” with high local pressure (e.g., 10,000 atm) and temperature (e.g., up to 10,000 K) [10]. During this process, highly reactive radicals of H and OH \cdot are engendered via homolysis of water as well as other surfactants or excited state species [11]. Due to the fact that bulk graphite involves several graphene sheets which are weakly bonded through van der Waals force, there is a great possibility for taking the advantage of a tremendous energy to break this force in graphitic structure. Although the electrochemical exfoliation [12, 13] and ultrasound-assisted exfoliation [14, 15] are extensively employed for preparation of graphene and its derivative, the review of ultrasound energy and cathodic electrochemical exfoliation process for high-yield graphene production has not been explored yet.

In this part, the experimental conditions and contemporary information for producing of graphene material are only considered, with a focus on combination of electrochemical exfoliation and sonochemistry approaches. In the following parts, we firstly present an overview of electrochemical exfoliation method, and the new technique consisting of cathodic exfoliation and sonochemistry will then be comprehensively discussed.

2. Electrochemical exfoliation

Electrochemical exfoliation is one of the top-down approaches using graphite electrode as graphene precursor, which can be categorized into anodic and cathodic methods based on the electric sign of the graphite electrode. **Figure 1** displays the schematics of cathodic and anodic exfoliation mechanism. In both methods,

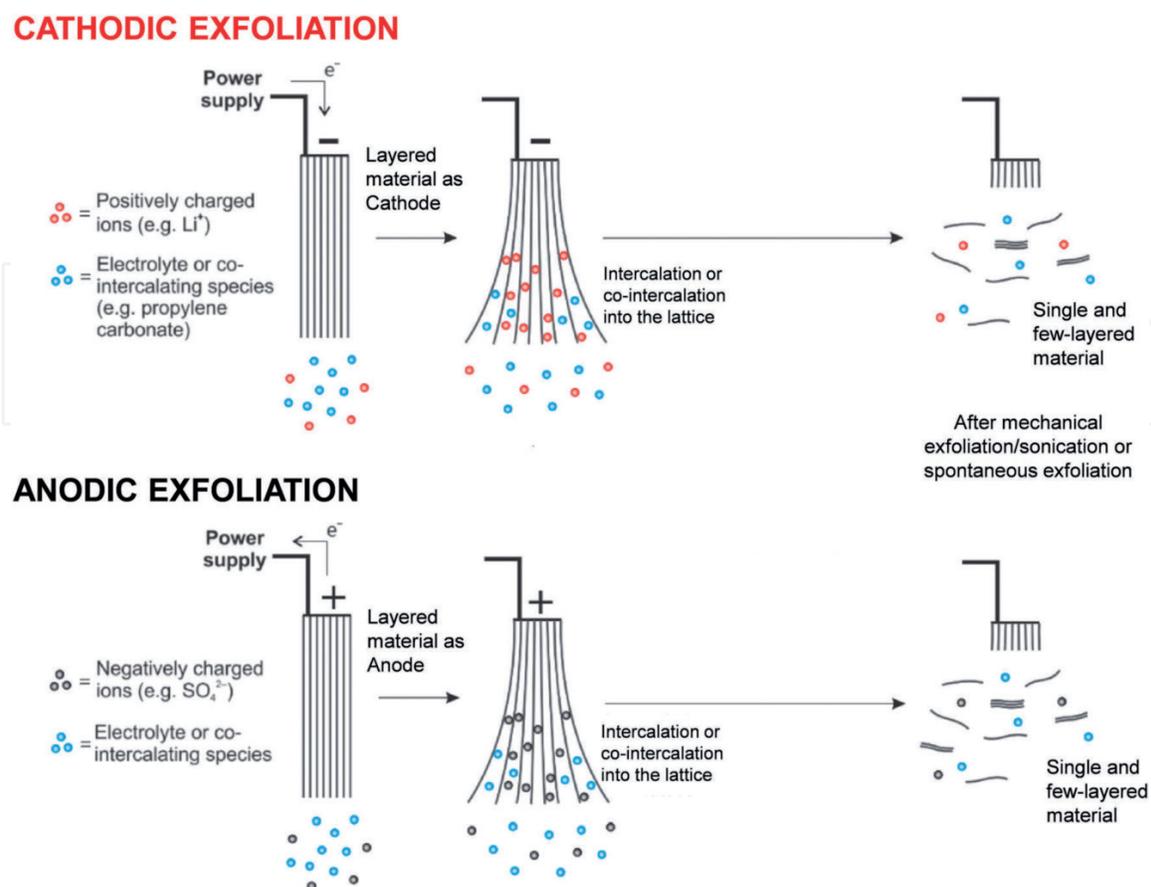


Figure 1. Mechanism for exfoliation of graphite by cathodic and anodic methods [16].

the oppositely charged intercalating ions and the co-intercalating molecules were attracted when a charging process was generated at the working electrode [16].

2.1 Anodic exfoliation

In this method, layered carbon material is applied with a positive voltage, which drives the intercalation of negative ions existing in the electrolytic solution. Different solvents and electrolytes were employed for the exfoliation of graphene:

2.1.1 Acidic electrolytes

Using highly oriented pyrolytic graphite (HOPG) electrode, different protonic acids such as HCl, HBr, and H₂SO₄ were used for electrochemical exfoliation of graphene [6]. Among the mentioned acids, H₂SO₄ has proven to be an appropriate electrolyte due to the highest efficiency; however, the graphene nanosheets were produced with high defects/orders in their structure. In order to reduce this effect, the electrolyte was prepared by adding of 98% H₂SO₄ solution and 20% KOH solution into 10 ml water. The system was firstly applied with low voltage of +2.5 V for 1 min, and higher potential of switching between +10 and -10 V was then applied until sufficient exfoliated material is obtained. During the process, the voltage of +10 V activates the exfoliation and oxidizes the graphene flakes. The oxidized graphene is then reduced when the voltage changed back to -10 V. **Figure 2** schematically illustrates the experimental setup, and the source of graphene acts as the anode for electrochemical exfoliation.

In another work, H₂SO₄, H₃PO₄, and H₂C₂O₄ were used as acidic electrolytes to synthesize graphene flakes using multiple electrochemical exfoliation (MEE) methods [13]. The process of synthesis graphene flakes from spent graphite rod is

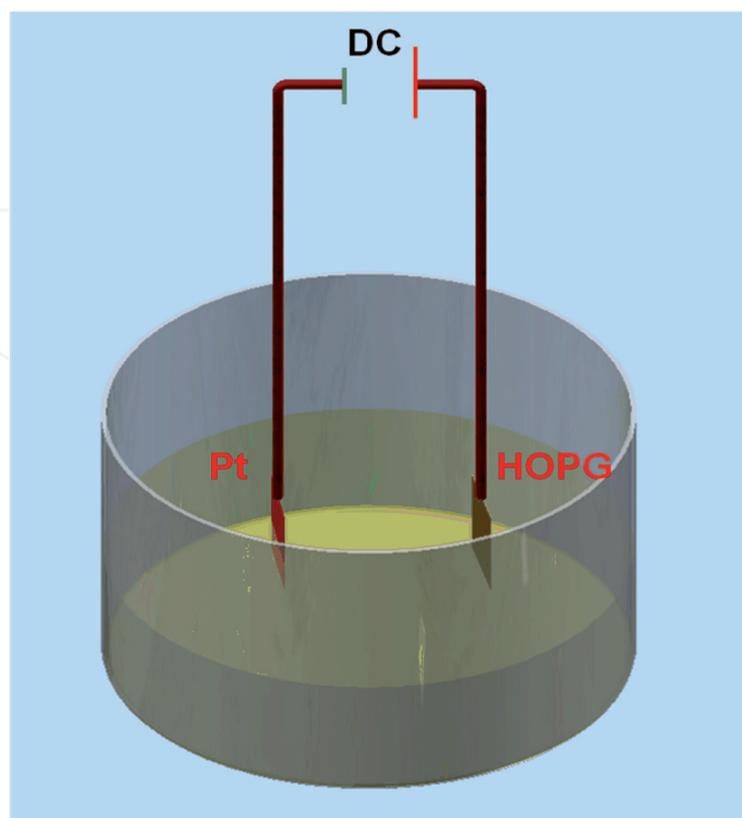


Figure 2.
Experimental setup for exfoliation of graphite by electrochemical method.

shown in **Figure 3**. In the electrochemical cell, the cathode platinum wire and the anode graphite rod were put at the top and the bottom, respectively. Upon applying a constant current at 0.1 A, the color of the solution changes gradually to black during the reaction time.

Several mild acids (i.e., phosphoric, sulfuric, oxalic, acetic, and formic acids) were employed as electrolytes for exfoliation of graphite [13]. Meanwhile, no observable exfoliation was detected in formic and acetic acids, possibly due to its small anions (e.g., HCOO^- and H_3CCOO^-), which results in delicate anion protection and weak expansion of graphite flakes due to ineffective intercalation of anion. Oxalic acid electrolyte is finally considered as the best choice because of its fast exfoliation and highly dispersed graphene in DI water. Furthermore, the product was easily purified by heating the exfoliated material in air.

2.1.2 Base electrolytes

There has been rare publication in electrochemical exfoliation of graphite in alkaline medium. A facile, environmentally friendly, and highly efficient exfoliation process was introduced by graphite electrolysis in a weak alkaline solution aqueous ammonium hydroxide (28–30 wt%) instead of acidic electrolyte or strong alkaline solution [17]. The graphite electrode was firstly subjected to an anodization treatment at 10 V for 30 min and subsequently treated by anodization at 10 or 5 V for 90 min. The exfoliation can be explained by the intercalation of nitrogen gas originating from the electrooxidation of ammonium hydroxide when electrolysis is performed in the alkaline electrolyte.

2.1.3 Salt electrolytes

The formation of graphite intercalation compounds (GIC) was firstly done with sulfuric acid [6]; however, sulfate ions were then realized to play a decisive role as an intercalant because all neutral salts of $(\text{NH}_4)_2\text{SO}_4$, Na_2SO_4 , and K_2SO_4 exhibited

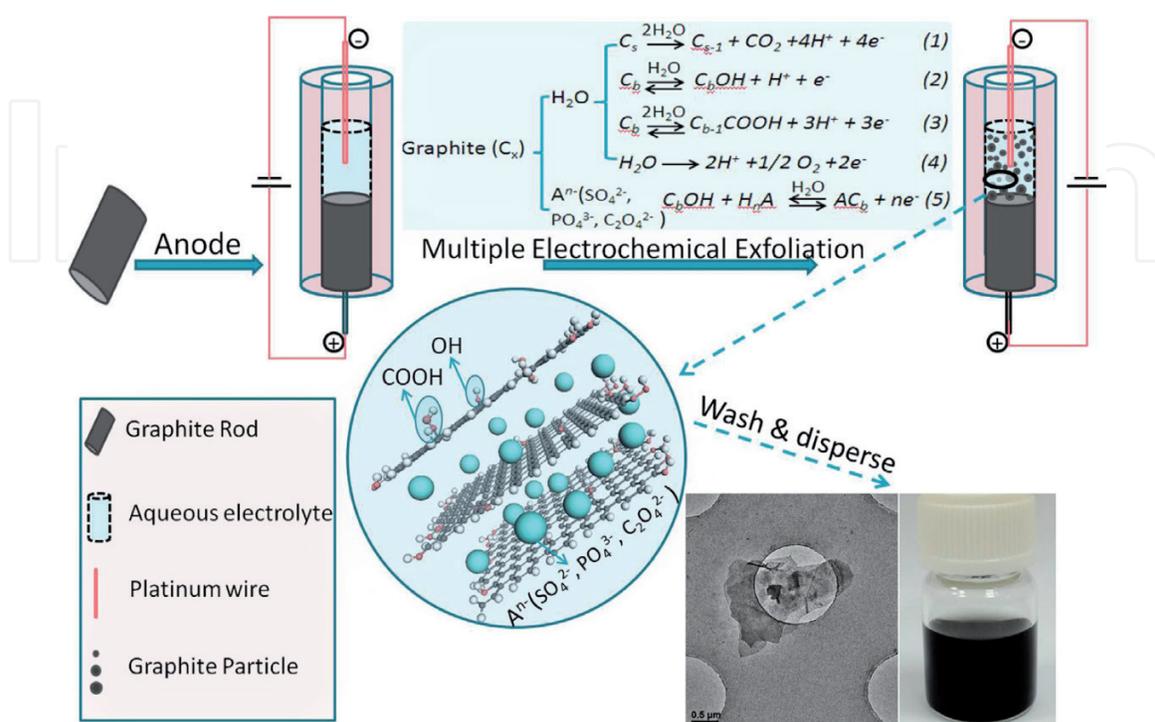


Figure 3. Experimental setup and mechanism for production of graphene by multiple electrochemical exfoliations [13].

pronounced exfoliation efficiency [12]. In addition, the superior activity of sulfate ions can be explained by its lower reduction potential to produce SO_2 (i.e., +0.20 V). In contrast, ClO_4^- and NO_3^- ions have high reduction potentials of 1.42 and 0.96 V, respectively, to generate Cl_2 and NO gases [12]. Therefore, it is suggested that graphite sheets are exerted with large and sufficient forces to isolate weakly bonded graphite layers from each other by SO_2 and O_2 gases generated in sulfate ion oxidation.

2.2 Surfactants

Due to very excellent intercalant role of sulfate anion, the organic derivatives of sulfate ion-sulfonates such as poly(sodium-4-styrenesulfonate), sodium dodecyl sulfate (SDS), and sodium dodecyl benzene sulfonate (SDBS) were also investigated for graphite exfoliation [18–20], which play a dual role of a surfactant as well as an intercalant. The additional advantage of using surfactants in the intercalation and exfoliation process is the stable graphene suspension production because surfactants can adsorb on the surface of produced graphene layers and prevent its reassembling [20]. **Figure 4** describes how SDS with a concentration of 0.1M works

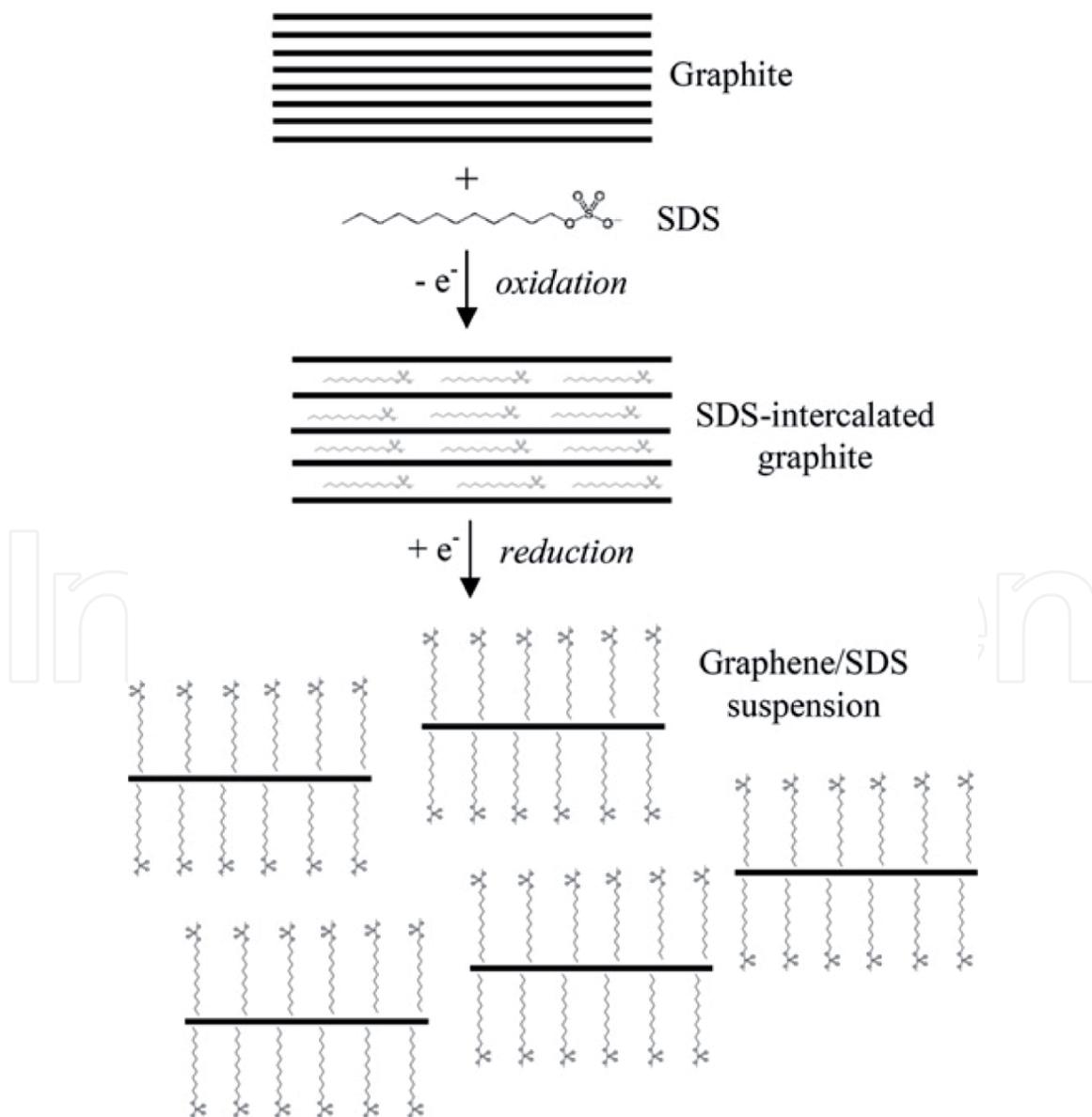


Figure 4.
Electrochemical method for graphene/SDS suspension production [20].

during graphene intercalation from the anode of graphite and exfoliation from cathode of SDS-intercalated graphite [20].

2.3 Cathodic exfoliation

The cathodic exfoliation process for graphene production has been introduced by several groups [21–24]. In this approach, the positive ions in electrolytes are intercalated into graphite interlayers by applying negative potential, which consequently facilitates their exfoliation. This process is accomplished by using either organic or aqueous solvents.

Wang et al. [21] used cathodic electrochemical exfoliation in liquid rechargeable lithium-ion batteries to prepare few-layer graphene flakes. They indicated that graphite interlayers can be intercalated by Li ions during the charging process. Subsequently, the complex was exfoliated to few-layer graphene flakes by sonication as shown in **Figure 5A**. They used a potential of -15 ± 5 V as cathodic charge in order to trigger off Li⁺ intercalation in graphite. The exfoliated graphene sheets had very low defects as confirmed by a small I_D/I_G ratio of 0.1 with of two to three layers of thickness and an average lateral size of 1–2 μm . Additionally, graphene nanosheets were directly obtained from electrochemical cathodic exfoliation under high negative voltages of 5–30 V using tetra-n-butylammonium (TBA) as organic electrolyte [22]. Yang et al. [22] have demonstrated that at the initial stage, the solvated TBA⁺ under highly negative voltage contributes to expand the layer spacing induced by the intercalation. The exfoliated graphene nanosheets exhibited high quality with the basal size of ~ 10 μm , three to six layers of thickness, and 0.34 nm of lattice spacing. In another example, a continuous of few-layer graphene production was developed by Abdelkader group [23] with mechanism displayed in **Figure 5B**. In their report, organic solvents and the electrolyte of lithium and alkylammonium ions (triethylammonium, Et₃NH⁺) in dimethyl sulfoxide (DMSO) were used. Interestingly, they found that not only lithium ions but also Et₃NH⁺ ions can be intercalated to enhance exfoliation efficiency. Furthermore, this cathodic exfoliation of graphite can avoid oxidation of graphite and decrease the defects, where few-layer graphene with no any oxidation and lateral size of 1–20 μm was produced without any sonication or centrifugation step, by using other kinds of intercalation ion such as AlCl₄⁻ and Al₂Cl₇⁻.

Lei et al. [24] produced graphene from graphite cathode in AlCl₃/EMImCl (1-ethyl-3-methylimidazolium chloride) ionic liquids using Al-ion battery. With voltage of >2.0 V, few-layer graphene can be achieved by cathodic electrolysis. The estimated mechanism for cathodic electrolytic exfoliation of graphite in ionic liquid is displayed in **Figure 5C**.

With a new term of direct cathodic exfoliation of graphite by plasma electrolysis, Thanh and his collaborators introduced a facile and rapid method to produce both graphite oxide and graphene nanosheets [25, 26]. **Figure 6A** shows the schematic of the experiment for producing plasma-electrochemically exfoliated graphene (PEEG) sheets, where high-purity graphite (HG) is employed for both the cathode and anode. The cathode tip is set above the aqueous electrolyte, while the anode is immersed in the electrolyte of KOH and (NH₄)₂SO₄ solution. A voltage of 60 V is applied to the system by using a DC power when the tip of cathode is immersed about 1 mm in the electrolytic solution. It is noticed that the cathode has much smaller surface area contacting to the electrolyte than the anode. As a result, a high electric field is generated at the submerged cathode tip and produces hydrogen gas bubbles via hydrolysis of water. A plasma phenomenon around the cathode tip is formed by the instant ionization of hydrogen caused by high electric field surrounding the cathode tip.

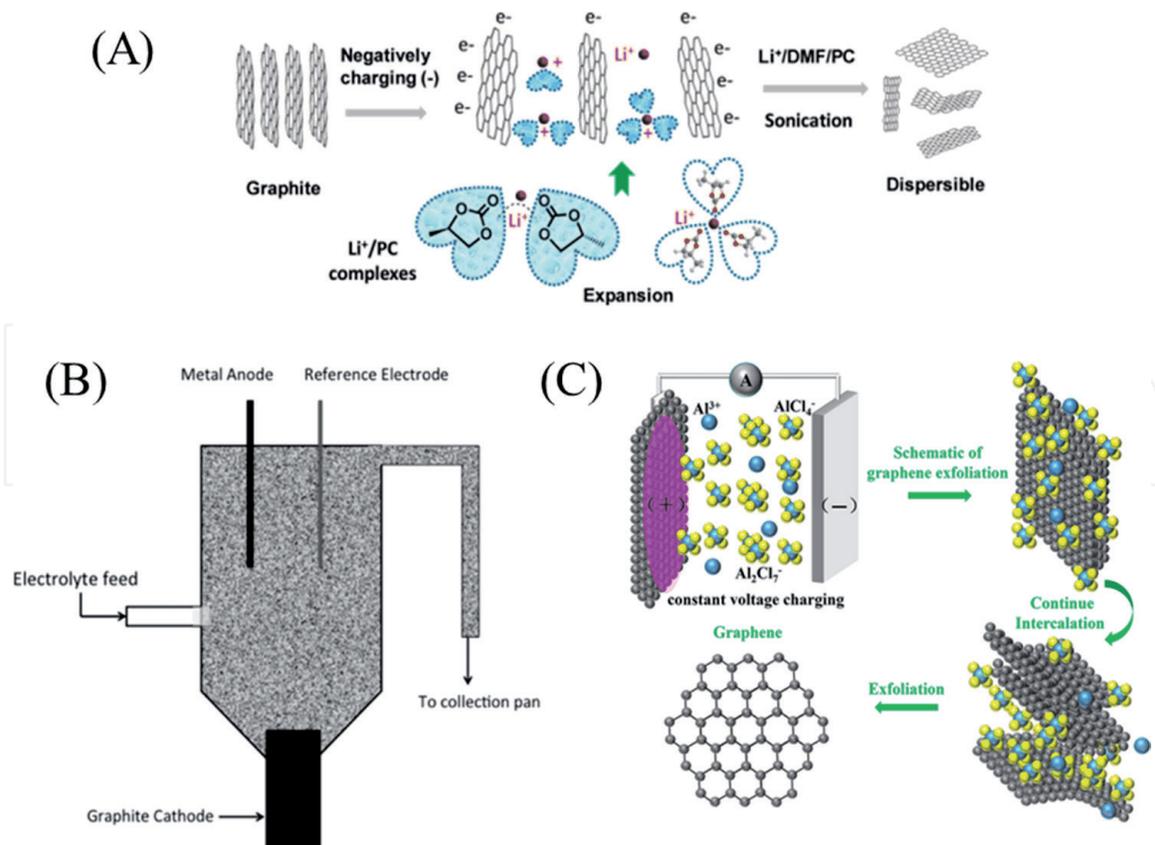


Figure 5. Schematics of (A) electrochemical cell for a continuous process [23], (B) graphite exfoliation in the Al-ion battery [24], and (C) graphite exfoliation via intercalation [21].

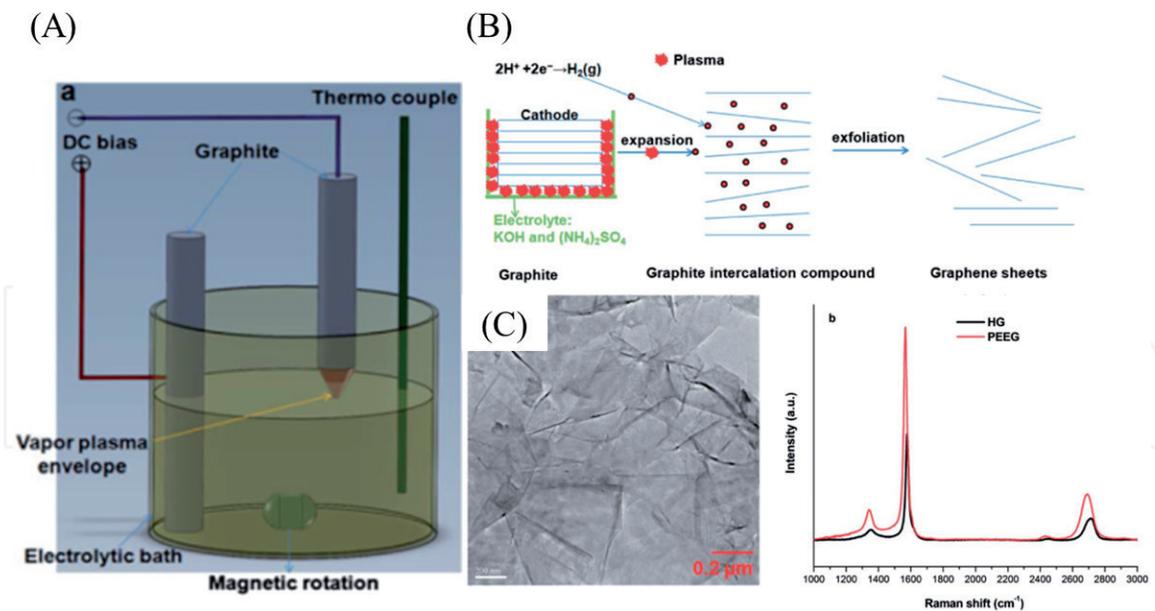


Figure 6. (A) Experimental setup for plasma-electrochemically exfoliated graphene sheet production, (B) proposed PEEG formation mechanism, and (C) TEM image and Raman spectra of PEEG [26].

The mechanism for exfoliation of graphene sheets from graphite cathodic rod is displayed in **Figure 6B**, which attributed that the exfoliation process is caused by hydrolyzed hydrogen bubbles produced at the cathode. The explosion of hydrogen around the cathode tip expands its surface edge, which enables the insertion of hydrogen molecules into the interlayer of the graphite sheets to form intercalated graphite compounds. Simultaneously, the high temperature (e.g. $\sim 2000^\circ C$) in

instant time (e.g. nanosecond) on the cathode tip during the discharge process gives thermo-mechanical stresses on the graphite surface, which produces graphene nanosheets from graphite rod. On the other hand, graphene sheets can also be yielded from graphite rod by the electrochemical reaction occurring at the anode in a basic electrolyte medium. As a comparison, plasma-assisted electrochemical exfoliation process can produce graphene sheets with high efficiency of ~6 times faster than the conventional electrochemical method at applied voltage of 10 V. The produced material is graphene sheets with high quality as presented in the TEM image of **Figure 6C**. The structure transformation from graphite to graphene sheets can be confirmed by Raman spectra (**Figure 6C**), where the weak D band peak located at 1353 cm^{-1} is more pronounced than that in the spectrum of HG. Moreover, the 2D band peak of PEEG at 2706 cm^{-1} is shifted to lower frequency, while the intensity of PEEG is higher than that of HG. This confirms the produced graphene structure with $\sim 2.5\text{ }\mu\text{m}$ in sheet lateral size and 2.5 nm in thickness. Interestingly, they also produced graphite oxide by this method in 2013 [25].

3. Ultrasonic-assisted cathodic electrochemical discharge exfoliation (UCEDE)

Cathodic plasma electrolysis, a combination of conventional electrolysis and plasma processes under ambient condition, employs a voltage that is much higher than that of traditional electrochemical method between two electrodes in an aqueous solution. Surface of one electrode, active electrode (workpiece, regardless of its role as anode or cathode), must be much smaller than that of the other. The method can be separated into anodic and cathodic plasma electrolysis (CPE) based on the opposition of applied voltage to the workpiece. Most of the researches have focused on the anodic regime of plasma electrolysis while little on the cathodic one [27]. CPE is principally based on the reaction or vaporization of electrolyte and the electrical breaking of gaseous envelope, resulting in the formation of sparks around the active electrode [27–29]. The comprehensive reviews of plasma electrolysis can be found in some excellent reviews [15, 25, 26].

The cathodic process has been applied for producing nitride, carbon, and other metals such as zinc, zinc-aluminum, molybdenum, and titanium-based coatings on the metal substrate [27–31]. The nanocrystalline graphite films on titanium substrate have been deposited by the cathodic plasma electrolysis from a predominant ethanol liquid phase [32, 33]. In fact, each layer of graphene in the bulk graphite is bound by weak van der Waals interactions to other two adjacent layers of hexagonally close-packed C atoms. Upon the impact on the surface as thermal extension or ultrasonication, it is readily exfoliated into separated graphene nanosheets. As a result, the plasma electrolysis phenomenon for production of graphene flakes and its derivatives is believed to be caused by the breaking of graphene layers from its bulk structure with weak van der Waals force.

Typically, using a mechanical mean such as ultrasonic after electrochemical intercalation and expansion of graphite is essential. During ultrasonication with pressure oscillations, the cavitation and shear forces, as well as the collapse of the bubbles or voids on liquid, could activate both graphite intercalation and expansion, which leads to a complete exfoliation. A new ultrasonic-assisted cathodic electrochemical discharge approach has been developed to exfoliate graphene nanosheets from graphite rod by using a combination of ultrasonic energy and in situ plasma-induced electrochemical exfoliation [15]. Without expensive ionic liquid or acidic media, this method revealed broad benefits such as direct production of graphene at ambient pressure and low temperature as well as a facile, environmentally

friendly, and fast process. **Figure 7** displays the experimental setup and an actual figure for production of ultrasonic-assisted in situ plasma-induced electrochemical exfoliation graphene (UPEEG).

The formation of plasma at high voltage of 60 V is initiated by the reduction to form hydrogen gas at cathode (Eq. 1) and the oxidation to form oxygen at anode (Eq. 2):



At appropriate voltage, the electrolyte near graphite cathode is vaporized because of the high electric field created by sharp point of cathode. This releases vigorous hydrogen around the graphite cathode tip and forms plasma zone between the cathode tip and the electrolytic solution.

Results from XPS and Raman analyses (**Figure 8A–C**) show the successful production of graphene via this method. It is believed that the positive ions surrounding the interface of electrolyte and HG tip could be speeded up directionally toward the cathode surface to implode on expanded position and to instantly exfoliate graphite at this point for graphene formation. In addition, the proposed mechanism for UPEEG formation from graphite is related to the expansion of the graphite tip in the plasma zone, where the graphene sheets were formed under the ultrasonic-assisted condition (**Figure 8D**). The extremely high-temperature outermost cathodic tip in the plasma zone leads to the expanding and cracking of graphite surrounding with weakening van der Waals forces. In this case, the violent fluctuation in the vapor plasma envelope and the cavitation from the sonication are

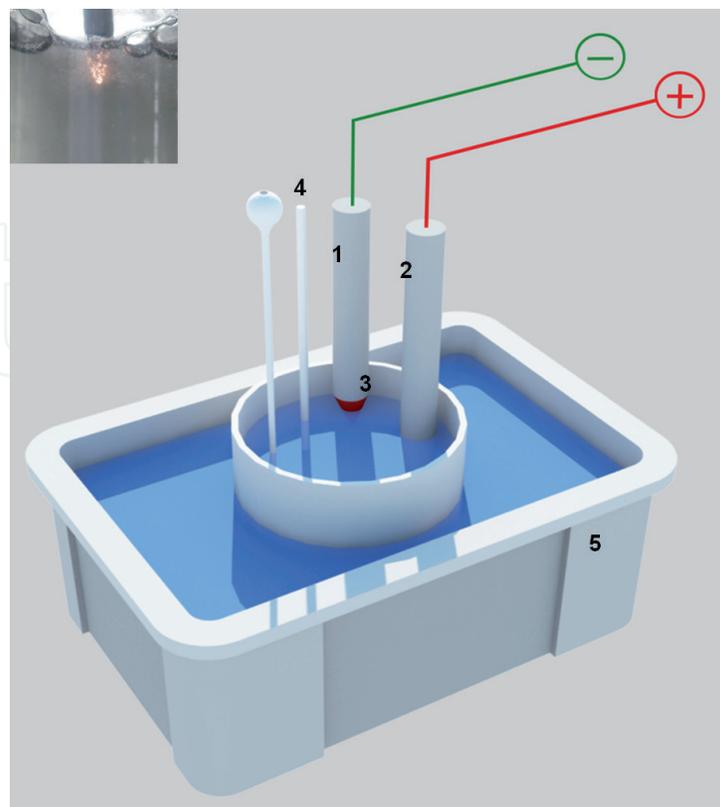


Figure 7. Experimental setup for production of UPEEG: (1) cathode, (2) anode, (3) vapor plasma envelope, (4) ultrasonic cleaner; inset is image of cathodic electrochemical discharge phenomenon [15].

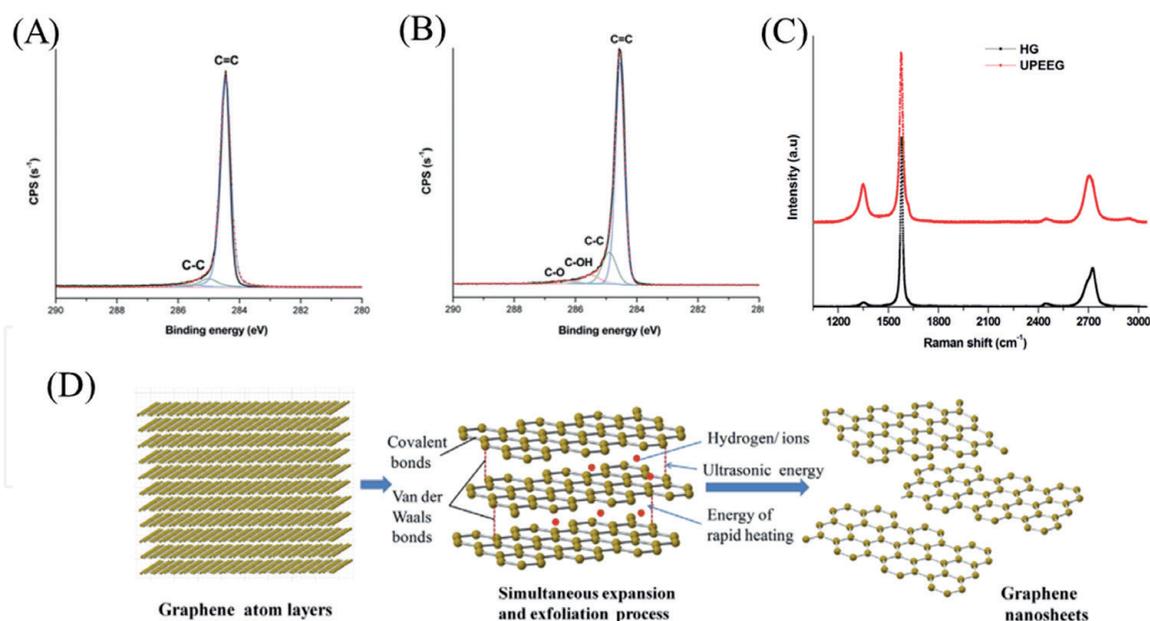


Figure 8. XPS C_{1s} spectra of (A) HG and (B) UPEEG; (C) Raman spectra of HG and UPEEG; (D) proposed mechanism for the formation of graphene sheets [15].

the main reasons for exfoliation of expanded layers. At first, the shear and shock wave in ultrasonic exfoliating fluid and the thermal expanded or cracked surface are engendered. Subsequently, the cavitation bubbles formed during sonication prompted the disturbance and pulling at the expanded and cracked points in the exfoliating fluid media. Next, the enlarged shear forces appear between neighboring layers and weaken van der Waals forces between layers. Finally, the expanded positions of the adjacent layers are penetrated and intercalated by the hydrogen atoms or ions, which consequently causes the breaking at these points and results in graphene exfoliation. Due to its high porosity of graphite lattice under high diffusion temperature, it can be diffused and intercalated by the hydrogen atoms. We think that this facile method will pioneer and create new possibilities for production of graphene sheets, graphite oxide, or doping graphene for a number of applications.

4. Conclusions

Sonoelectrochemical exfoliation of graphite is a potentially scalable way to achieve high quality and high quantity of graphene production by using simple equipment that is almost available in all chemistry laboratories. From the point of technology view, the electrochemical exfoliation with the aid of ultrasonication is dual benefited not only to easy-to-break van der Waals forces but also to the effective inhibition of the agglomeration of produced graphene nanosheets. Moreover, the presence of ultrasonication herein can accelerate and promote the exfoliation process.

In this chapter, we discussed on the synthesis of high-quality graphene by direct ultrasonic-assisted cathodic electrochemical exfoliation process. Immense works have been done in order to control and enhance the yield and oxidation degree of graphene sheets. However, the yield of graphene sheets in a single layer is still relatively limited and requires long periods of sonication time with massive heat release into the environment. In the short run, the improvement and design optimization on reproducible protocol should be devoted to define the best condition for sonoelectrochemical exfoliation method. Besides, one might seem very presumably that the unreasonable reaction should be existed that taking into account for the

formation and exfoliation of graphene nanosheets and their functional groups containing oxygen on the surface. The mechanism is still in its infancy and should be unveiled in the near future to pave the way for controlling of graphene production and its derivatives. Therefore, we hope this chapter will contribute critical insights for understanding the graphene synthesis and hence can open an alternative approach toward 2D materials in general and graphene material in specific.

IntechOpen

Author details

Nguyen Van Truong¹, Nguyen Quoc Dung², Nguyen Nhat Huy³, Pham Van Hao⁴
and Dang Van Thanh^{5*}

1 Faculty of Fundamental Science, Thai Nguyen University of Technology, Vietnam

2 Department of Chemistry, Thai Nguyen University of Education, Vietnam

3 Faculty of Environment and Natural Resources, Ho Chi Minh City University of Technology, VNU-HCM, Vietnam

4 Faculty of Basic Science, TNU-University of Information and Communication Technology, Vietnam

5 Faculty of Basic Science, TNU-University of Medicine and Pharmacy, Vietnam

*Address all correspondence to: thanhdv@tnmc.edu.vn

IntechOpen

© 2019 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 

References

- [1] Yi M, Shen Z. A review on mechanical exfoliation for the scalable production of graphene. *Journal of Materials Chemistry A*. 2015;**3**:11700-11715. DOI: 10.1039/c5ta00252d
- [2] Li X, Yu J, Wageh S, Al-Ghamdi AA, Xie J. Graphene in photocatalysis: A review. *Small*. 2016;**12**:6640-6696. DOI: 10.1002/smll.201600382
- [3] Bonaccorso F, Colombo L, Yu G, Stoller M, Tozzini V, Ferrari AC, et al. Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage. *Science*. 2015;**347**: 1246501-1246509. DOI: 10.1126/science.1246501
- [4] Liu L, Corma A. Metal catalysts for heterogeneous catalysis: From single atoms to nanoclusters and nanoparticles. *Chemical Reviews*. 2018;**118**:4981-5079. DOI: 10.1021/acs.chemrev.7b00776
- [5] Hummers WS, Offeman RE. Preparation of graphitic oxide. *Journal of the American Chemical Society*. 1958;**80**:1339. DOI: 10.1021/ja01539a017
- [6] Su CY, Lu AY, Xu Y, Chen FR, Khlobystov AN, Li LJ. High-quality thin graphene films from fast electrochemical exfoliation. *ACS Nano*. 2011;**5**:2332-2339. DOI: 10.1021/nn200025p
- [7] Compton RG, Eklund JC, Marken F. Sonochemical processes: A review. *Electroanalysis*. 1997;**9**:509-522. DOI: 10.1002/elan.1140090702
- [8] Bang JH, Suslick KS. Applications of ultrasound to the synthesis of nanostructured materials. *Advanced Materials*. 2010;**22**:1039-1059. DOI: 10.1002/adma.200904093
- [9] Xu H, Zeiger BW, Suslick KS. Sonochemical synthesis of nanomaterials. *Chemical Society Reviews*. 2013;**42**:2555-2567. DOI: 10.1039/c2cs35282f
- [10] Peller J, Wiest O, Kamat PV. Sonolysis of 2,4-dichlorophenoxyacetic acid in aqueous solutions. Evidence for OH-radical-mediated degradation. *The Journal of Physical Chemistry A*. 2002;**105**:3176-3181. DOI: 10.1021/jp003478y
- [11] Suslick KS, Price GJ. Applications of Ultrasound to Materials Chemistry. *Annual Review of Materials Science*. 1999;**29**:295-326. DOI: 10.1146/annurev.matsci.29.1.295
- [12] Parvez K, Wu ZS, Li R, Liu X, Graf R, Feng X, et al. Exfoliation of graphite into graphene in aqueous solutions of inorganic salts. *Journal of the American Chemical Society*. 2014;**136**:6083-6091. DOI: 10.1021/ja5017156
- [13] Liu J, Poh CK, Zhan D, Lai L, Lim SH, Wang L, et al. Improved synthesis of graphene flakes from the multiple electrochemical exfoliation of graphite rod. *Nano Energy*. 2013;**2**:377-386. DOI: 10.1016/j.nanoen.2012.11.003
- [14] Lee H, Bratescu MA, Ueno T, Saito N. Solution plasma exfoliation of graphene flakes from graphite electrodes. *RSC Advances*. 2014;**4**:51758-51765. DOI: 10.1039/c4ra03253e
- [15] Van Thanh D, Oanh PP, Huong DT, Le PH. Ultrasonic-assisted cathodic electrochemical discharge for graphene synthesis. *Ultrasonics Sonochemistry*. 2017;**34**:978-983. DOI: 10.1016/j.ultsonch.2016.07.025
- [16] Yu P, Lowe SE, Simon GP, Zhong YL. Electrochemical exfoliation of graphite and production of functional graphene. *Current Opinion*

in Colloid & Interface Science. 2015;**20**:329-338. DOI: 10.1016/j.cocis.2015.10.007

[17] Chang LC, Hsieh YC, Chen YM, Wu PW, Lee JF. Fabrication of graphene by electrochemical exfoliation in alkaline electrolytes. ECS Transactions. 2014;**58**:33-38. DOI: 10.1149/05824.0033ecst

[18] Wang G, Wang B, Park J, Wang Y, Sun B, Yao J. Highly efficient and large-scale synthesis of graphene by electrolytic exfoliation. Carbon. 2009;**47**:3242-3246. DOI: 10.1016/j.carbon.2009.07.040

[19] Joo EH, Kuila T, Kim NH, Lee JH, Kim SA, Park EG, et al. Electrochemically preparation of functionalized graphene using sodium dodecyl benzene sulfonate (SDBS). Advanced Materials Research. 2013;**747**:246-249. DOI: 10.4028/www.scientific.net/AMR.747.246

[20] Alanyalıoğlu M, Segura JJ, Oró-Solè J, Casañ-Pastor N. The synthesis of graphene sheets with controlled thickness and order using surfactant-assisted electrochemical processes. Carbon. 2012;**50**:142-152. DOI: 10.1016/j.carbon.2011.07.064

[21] Wang J, Manga KK, Bao Q, Loh KP. High-yield synthesis of few-layer graphene flakes through electrochemical expansion of graphite in propylene carbonate electrolyte. Journal of the American Chemical Society. 2011;**133**:8888-8891. DOI: 10.1021/ja203725d

[22] Yang Y, Ji X, Yang X, Wang C, Song W, Chen Q, et al. Electrochemically triggered graphene sheets through cathodic exfoliation for lithium ion batteries anodes. RSC Advances. 2013;**3**:16130-16135. DOI: 10.1039/c3ra43010c

[23] Abdelkader AM, Kinloch IA, Dryfe RAW. Continuous

electrochemical exfoliation of micrometer-sized graphene using synergistic ion intercalations and organic solvents. ACS Applied Materials & Interfaces. 2014;**6**:1632-1639. DOI: 10.1021/am404497n

[24] Lei H, Tu J, Yu Z, Jiao S. Exfoliation mechanism of graphite cathode in ionic liquids. ACS Applied Materials & Interfaces. 2017;**9**:36702-36707. DOI: 10.1021/acsami.7b03306

[25] Van Thanh D, Chen H-C, Li L-J, Chu C-W, Wei K-H. Plasma electrolysis allows the facile and efficient production of graphite oxide from recycled graphite. RSC Advances. 2013;**3**:17402. DOI: 10.1039/c3ra43084g

[26] Van Thanh D, Li L, Chu C, Yen P, Wei K. Plasma-assisted electrochemical exfoliation of graphite for rapid production of graphene sheets. RSC Advances. 2014;**4**:6946. DOI: 10.1039/c3ra46807k

[27] Aliofkhazraei M, Rouhaghdam AS, Gupta P. Nano-fabrication by cathodic plasma electrolysis. Critical Reviews in Solid State and Materials Sciences. 2011;**36**:174-190. DOI: 10.1080/10408436.2011.593269

[28] Gupta P, Tenhundfeld G, Daigle EO, Ryabkov D. Electrolytic plasma technology: Science and engineering: An overview. Surface and Coating Technology. 2007;**201**:8746-8760. DOI: 10.1016/j.surfcoat.2006.11.023

[29] Yerokhin AL, Nie X, Leyland A, Matthews A, Doney SJ. Plasma electrolysis for surface engineering. Surface and Coating Technology. 1999;**122**:73-93. DOI: 10.1016/S0257-8972(99)00441-7

[30] Gupta P, Tenhundfeld G, Daigle EO, Schilling PJ. Synthesis and characterization of hard metal coatings by electro-plasma technology.

Surface and Coatings Technology.
2005;**200**:1587-1594. DOI: 10.1016/j.
surfcoat.2005.08.030

[31] Nie X, Tsotsos C, Wilson A,
Yerokhin AL, Leyland A, Matthews A.
Duplex surface treatments combining
plasma electrolytic nitrocarburising
and plasma-immersion ion-assisted
deposition. Surface and Coatings
Technology. 2001;**139**:135-142. DOI:
10.1016/S0257-8972(01)01025-8

[32] Paulmier T, Bell JM, Fredericks PM.
Deposition of nano-crystalline graphite
films by cathodic plasma electrolysis.
Thin Solid Films. 2007;**515**:2926-2934.
DOI: 10.1016/j.tsf.2006.08.027

[33] Campos CS, Spada ER, De Paula FR,
Reis FT, Faria RM, Sartorelli ML. Raman
and XRD study on brookite-
anatase coexistence in cathodic
electrosynthesized titania. Journal of
Raman Spectroscopy. 2012;**43**:433-438.
DOI: 10.1002/jrs.3048