Synthesis of graphene oxide via electrochemical process: A short review towards flexible synthesis method

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Abstract. Graphene-based material for instance graphene oxide (GO) and reduce graphene oxide (rGO) emerge as unique frontier material that has been widely applied in various application such as energy conversion, nanotechnology as well as oil and gas industry. It properties such as high mechanical properties and enhance electrical conductor have made this material outperforms existing frontier material thus features large-scale commercialization opportunity. At present, electrochemical method has attracted much attention in synthesizing graphene-based material (GO/rGO) due to its green technology (environmentally friendly process), low cost and enhanced efficiency. Nevertheless, based on contemporary studies, different demand in GO/rGO quality requires different parametric setup and characterization analyses subsequently provides significant challenge to identify a standard design of electrochemical that can produce various quality of GO/rGO. This inflexibility affects the progress of commercial scale-up thus entails a systematic review related to various aspects of electrochemical studies for instance parametric analysis, product/material characterization and applications. A parametric analysis includes electrolyte concentration, type of electrolyte, temperature, synthesis time, cathode and anode materials and voltage demand. While, for product characterization, several methods are evaluated for instance Transmission electron microscopy (TEM) and Raman spectroscopy (RAMAN). This review paper is beneficial to the researcher and industries as a rapid guideline towards the flexible mass-production of GO/rGO via electrochemical method. Finally, future research should be conducted on the flexible design of unit operation (i.e. reactor) to ensure process feasibility.

1. Introduction

Graphene and graphene oxide (GO) is not notoriously known to the public but it is foreseen to be the wonder material in 21st century just as plastic was considered crucial in the 20th century development. This prevision is manifested by the potential of graphene-based materials for application in different fields due to their unique physical and chemical properties such as its outstanding electronic, mechanical, optical, and thermal properties. A GO and reduce-GO (rGO) are the main research branches and exhibited as a great precursor to synthesis graphene with higher yield and lower synthesising costs. GO is a material that consisted of a single monomolecular layer of graphite with various oxygen contained functionalities, such as OH, C=O and C-O-C groups. While, rGO is a graphene-like sheets by removing the oxygen-containing groups with the recovery of a conjugated structure [1].

The presence of oxygen functionalities in GO makes GO easily disperse in water and organic solvents. This advance property make GO have benefit as an additive on ceramic and polymer manufacturing
process in enhancing their electrical and mechanical properties such as tensile strength, elasticity and conductivity [2]. Furthermore, GO/rGO plays a significant role in energy storage and conversion due to its efficient thermal and electrical conductor [3]. Several methods have been explored to determine the best route to synthesis GO/rGO such as the Modified/Improved Hummers method [4-6], chemical vapor deposition (CVD) [7, 8] and microwave irradiation system [9-11].

At present, electrochemical method has attracted much attention in synthesizing graphene-based material (in this review, graphene based materials are described as graphene, GO and rGO and its composites) due to its green technology (environmental friendly process), low cost and enhanced efficiency. Nevertheless, based on contemporary studies, different demand in GO/rGO quality requires different parametric setup and characterization analyses subsequently provides significant challenges to identify a standard design of electrochemical process that can produce various quality of graphene-based material without require huge process modification and extensive characterization studies. Similar comment has been reported by Achee et al. [12], whereas production of graphene-based material features lack of standardization.

This work focuses solely on the recent progress of graphene-based material from electrochemical exfoliation method with the aim to find a measure for the aforementioned limitation/challenge. The literatures analyses involve evaluation of curated articles from year 2010 until 2020, which encompasses of various scientific and technical databases. Quality of graphene based material (product) is discussed based on the optimal operating condition and characterization analyses. Finally, present work proposes facile and flexible design of experiment to synthesis the graphene based material at rapid way.

2. Flexible operation of electrochemical exfoliation process

In electrochemical process, graphene-based material is synthesized via graphite conductivity by stimulating the anions/molecules in the electrolyte into graphite subjected to the voltage/current biases, in order to form a graphite intercalation compound. Electrolyzed water which produce oxygenated material will oxidize the graphite intercalation compound to form GO/rGO. Electrochemical exfoliation of GO/rGO from graphite involves two possible alternative routes such as single-step and two-step electrochemical processes, which consists of anodic and cathodic graphite exfoliation mechanisms. Many reviews have been done related to the electrochemical exfoliation process of graphene-based material. Liu et al. [13] have reviewed existing articles related to GO synthesis in term of operating condition of electrochemical exfoliation process, product quality and characterization studies. Their review suggested to emphasize on the fundamental of graphite mechanism in exfoliation process to obtain good quality of graphene-based material, to promote large-scale setup and to determine possible application of graphene-based material in the emerging application. Lee et al. [14] summarized the characterization analyses related to the prevailing synthesis methods of graphene/GO and its derivative with the additional analyses including production cost and yield. Similarly, Le et al. [15] have conducted a review study which combine similar scopes of work as in [13, 14]. Three different methods have been discussed in their review paper, such as two-electrode, three-electrode and electrolyte exfoliation. These trends evident a novelty of this short review article whereas to the best of author knowledge, there is no study proposes a standard electrochemical exfoliation method to accommodate different industrial and product demands. To narrow down the scope of this review, we only select studies involved with platinum as the counter electrode, as tabulated in Table 1. Since platinum is known as a feasible and flexible electrode that can accommodate different type of working electrode.

2.1 Single step electrochemical exfoliation process

Single step electrochemical method involves intercalation of electrolyte ion to produce graphene. Sharif et al. [16] has successfully synthesized a monolayer and bilayer graphene via single-step exfoliation (direct) mechanism. In their work, a minimum defect of as synthesized graphene with high temperature
stability in air was produced by using ammonium sulphate as an electrolyte at a voltage of 10 V for 3 h synthesis time. Chen et al. [17] used similar electrolyte solution at a voltage of 10 V with low concentration (0.1 M) to produce graphene from pencil core. Other studies have shown that utilization of ammonium sulphate as the electrolyte is able to produce a thin layer of graphene [17, 18]. Jibrael et al. [19] used three different types of electrolyte solutions (sulfuric acid, nitric acid and distilled water) at voltage of 10 V for 50 min to produce graphene powder. On the other hand, Aghamohammadi et al. [20] used combination of hydrogen fluoride and titanium oxide to produce multi-layered graphene at a voltage of 10 V. They observed that addition of titanium oxide may enhance the exfoliation rate as well as promoting fluorination of graphene sheet as a composite material.

Prakoso et al. [21] produced graphene sheet via graphite extracted from spent Zn–C batteries. The electrochemical exfoliation process was conducted at a voltage of 5 V in a poly (sodium 4-styrenesulfonate) (PSS) solution. It was observed that they managed to produce high quality of graphene flakes using battery waste. Wang et al. [22] synthesized low defect of graphene layer by using graphite electrode coated with paraffin. In their work, concentrated sodium hydroxide was used as the electrolyte at voltage of 3 V under the confined space to promote exfoliation and to prevent excessive expansion of graphite. Similar concept was adapted by Achee et al. [12] where they demonstrated that utilization of compressed graphite powder can promote continuous intercalation, expansion and exfoliation simultaneously to ease the synthesis of graphene. In their work, high yield of graphene was successfully produced with large lateral size by using sulfuric acid as the electrolyte solution.

A well-oxidized monolayer GO have been synthesized by [12, 23, 24] using high concentration of sulphuric acid via exfoliation mechanism. In a different study, addition of surfactant into the electrolyte solution is able to produce GO via single step method. Nurhafizah et al. [25] managed to synthesis GO by using a sodium dodecyl sulphate (SDS) surfactant at a voltage of 10 V for 24 h synthesis time. Their as synthesized GO exhibited thinner sheet with wrinkles structures. Alternatively, different concentration of SDS surfactant from 0.001 to 1.0 M was analysed by Md Disa et al. [26]. They observed that the lowest GO production is given by the lowest concentration of SDS used which is 0.001 M. It can be seen, that only few studies have employed single-step electrochemical exfoliation process to obtained GO/rGO. Where, synthesis of graphene is more favourable to use this method.

2.2 Two-step electrochemical exfoliation process

Two-step electrochemical exfoliation process represents the intercalation and oxidation/exfoliation mechanisms in a sequential way. Chernysheva et al. [27] employed two-step mechanism to produce GO. First stage involved an anodic intercalation of graphite anode in sulfuric acid followed by the oxidation/exfoliation of the graphite in ammonium sulphate at a voltage of 10 V for 10 min. Shen et al. [28] found an optimal condition of GO synthesis at voltage of 2 V during intercalation process and 20 V during oxidation stage. Both stages were using high concentration of sulphuric acid (95% and 65%) at 10 min and 1 min synthesis time, respectively. Cao et al. [29] employed similar electrolyte solutions as in [28] at slightly lower voltage (10 V) to synthesis GO. Their two-step approach led to GO with a high yield (> 70 wt %), good quality (> 90%, monolayer), and reasonable oxygen content (17.7 %). High yield of GO using water electrolytic oxidation of graphite was conducted by Pei et al. [30]. Their study used high concentrated of sulfuric acid without oxidant agent for intercalation process followed by diluted sulfuric acid for oxidation process. It was observed that highly oxidized GO (C/O < 2) was achieved only when the sulfuric acid concentration is in the range of 40 wt.% to 60 wt.%

Contrary, Kumar et al. [31] used mixture of sulfuric acid and phosphoric acid for intercalation process followed by the oxidation process using potassium permanganate. High quality of GO was obtained based on their experimental condition at 6 h synthesis time with fix intercalation time at 4 min. Sahoo et al. [24] applied different concentration of sulfuric acid at 1 cm gap between two electrodes positions. Initial synthesis involved cathodic pretreatment of working electrode at a negative direct current (DC)
of 10 V for 30 s followed by 3 V for 15 min to ensure the expansion of pyrolytic graphite electrode for efficient intercalation process. Their result showed that low concentration of electrolyte (0.5 and 1.0 M sulfuric acid) was capable to stimulate the rate of electrochemical oxidation reactions at the graphite-electrolyte interface which exhibited more oxidation endowment in the product. This condition may contribute to the highest GO yield as correlated by [26].

Other studies have evident that utilization of sulfuric acid, at low synthesizing temperature are able to produce good quality of single/multilayer graphene/graphene based material [30, 32, 33]. For instance, moderate number of GO powder was synthesized using voltage of 2 V for 10 min intercalation process, followed by 60 s in the oxidation process (20 V). In their work, 65% sulfuric acid was used as an electrolyte at room temperature [32]. At the aforementioned condition, the as synthesized GO powder featured a single layer at 0.345 nm. A longer synthesizing time was conducted by Konwar et a. [33], where they managed to produce a highly pure GO in 0.1 M sulfuric acid solution at room temperature at constant potential of 3 V for 4 h. In a separate study, a monolayer of GO sheet with no defects or oxidation-containing functional groups was obtained by Pei et al. [30]. In their study, a concentrated sulfuric acid at 1.6 V (for 20 min) was used followed by the electrochemical reaction in 50% sulfuric acid for 3 min (5 V). Table 1 summarizes the operational condition of electrochemical synthesis of graphene based using platinum and counter electrode. Based on these two methods, it can be predicted that propose standard design to synthesis graphene-based material is via two-step method at 10 V (< 15 min) and 2 V (< 5 min) for intercalation and oxidation processes, using moderate concentration of sulfuric acid.

3. Characterization analysis of graphene based material

A GO's complex structure causes it difficult to suggest a standardize characterization method. For certain applications, different characteristics of GO are more significant than in others. Such characteristics are lateral scale, degree of oxidation, level of exfoliation, amount of moisture, categories of functional groups and the existence of impurities from the oxidation phase. These involve stacking of the GO, the lateral proportions of the GO, the functional groups found within/on the GO, and the degree of GO sheet disorder. In characterization analyses, stacking spacing is identified by XRD, while lateral proportions may be measured through methods such as FESEM, FETEM, AFM or optical microcopy, while RAMAN, FTIR or XPS indicate the functional groups present.

In this review, four characterization analyses are reviewed which include FESEM, XRD, FTIR, FETEM and RAMAN. These five characterization analyses are selected based on the frequency distribution study shown in Figure 1. Based on the figure, it can be seen that the common analysis that used to characterize graphene-based material (GO/rGO) are those four.

A crumpled sheets of GO was observed in FESEM analysis when using moderate to high concentration of surfactant electrolyte (0.1 - 1.0 M) while, thick agglomeration of GO was exhibited when low concentration (0.001 M) of surfactant was used [25]. In a different study, a highly-wrinkled of GO sheet was formed under the moderate concentration of sulfuric acid (65%) [35], which corroborate with the previous work done by [25]. Those structure indicates a deformation of the graphene layers due to the linkage of the oxygenated functional groups. Contrary, a large silk veil morphology with slightly folded edges and loose open structure was observed in GO composited with nanofibers when using 0.1 maniline and 1 M sulfuric acid mixed solution [34].

The XRD analysis is used to determine possible changes in the interlayer spacing. For instance, as synthesized GO produced by [35] showed a peak in the range of 9 – 12° corresponding to the (001) reflection plane. An intense and sharp peak at 20 = 11.66° was revealed which corresponds to the (001)
reflection plane [34]. The presence of this characteristic peak exhibited a completely oxidized GO during the electrochemical process.

Study conducted by Deiz-Pascual et al. [32] showed that C/O analysis was corroborate with the EDX analysis, elemental and FTIR analysis which exhibited a homogeneous and good quality of GO sheets, with a clear flake structure and lack of traces from the raw material. The darker areas in the FETEM analysis illustrated a good level of exfoliation, where thickness will be increased when with the increment of C/O ratio at decreasing of oxygen level. A TEM image for a mixed electrolyte solution with the typical 6-fold symmetric diffraction patterns with strong spots indicated the crystalline nature [16]. Similar TEM image pattern can be indicated in the study done by Chen et al. [18]. Where, both GO layers were synthesized using mixed electrolyte. Pei et al. observed that TEM image has consistent result with the AFM analysis [30]. It showed that about 46% of them are monolayer and about 86% are no more than three layers, which are consistent with the AFM measurement results.

Based on Raman spectroscopy, superior quality of graphene-based material (GO/rGO composite/derivative) can be exhibited at D, 2D and G peaks respectively. A typical D peaks can be observed at about 1323 cm⁻¹ [31], 1354 cm⁻¹ [35], 1360 cm⁻¹ [34] and 1363 cm⁻¹ [18]. Essentially, the D band arises from breathing mode of the sp² [16, 30] and attributed by defects or lattice disorders crystal structure due to the binding of oxygen-functional groups [35]. On the other hand, 2D peak is indicated at peak of 1600 cm⁻¹ [34] and 2650 cm⁻¹ [31] and usually attributed to second order phonon processes [35]. While, a typical G peak usually at about 1580 cm⁻¹ [16, 36], 1586 cm⁻¹ [35], 1590 cm⁻¹ [18] and 2700 cm⁻¹ [34]. It resembles to the in-plane vibration of sp² carbon atoms [16] with vibrational mode found in a graphite single crystal [37].

4. Conclusion and Outlook

This review paper could be used to conclude that electrochemical synthesis of GO is becoming a more common synthesis route to obtain graphene based material. It was also evident that in modern material science, graphene based material is a material that may be of significant use in the future since it can apply in various applications. That being the case, the outlook of this review would be to somehow create an idea for the common electrochemical setup for the synthesis of graphene-based material and also to increase the possibility of making the electrochemical route an ideal one.

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Table 1: Summary of operational condition of electrochemical synthesis of graphene based material using platinum as the counter electrode

| Ref  | Working electrode       | Counter Electrode | Power supplies (V) | Electrolyte                                      | Exfoliation time | T (℃) | Characterization analyses       | Type of graphene based material                      |
|------|-------------------------|-------------------|--------------------|-------------------------------------------------|------------------|-------|---------------------------------|------------------------------------------------------|
| [16] | Graphite sheet          | Platinum          | 10 (DC)            | Na$_2$SO$_4$, NH$_4$NO$_3$, (NH$_4$)$_2$SO$_4$, (NH$_4$)$_2$HPO$_4$ | 3-4 h            | 700   | TEM, RAMAN, XPS, AFM             | Graphene                                             |
| [38] | Graphite foil           | Platinum          | 1.1 or 2           | H$_2$SO$_4$                                      | 10 or 30 min     | 25 ± 2 | TEM, SEM, AFM, RAMAN, FTIR      | Single-layered GO sheets                              |
|      |                         |                   | 2.10 to 30         |                                                 | 30 and 120 s     |       |                                 |                                                      |
| [39] | Graphite                | Platinum          | 2                  | H$_2$SO$_4$, KNO$_3$, Phosphate Buffer           | -                | 25 ± 2 | SEM                             | Graphene oxide/cobalt oxide nanocomposite            |
| [40] | Pencil graphite electrode (PGE) | Platinum | 1                  | H$_2$SO$_4$, KNO$_3$, Phosphate Buffer           | -                |       | SEM                             | Graphene/Pt and graphene/Au tubular microengines    |
|      |                         |                   | 2                  |                                                 | -                |       |                                 |                                                      |
| [41] | Graphite                | Platinum          | -1.2 to +0.3       | 0.1 M H$_2$SO$_4$                                | -                | 25 ± 2 | SEM, EDX, CV                    | Magnetic functional graphene oxide (MFGO) nanocomposite |
|      |                         |                   |                    |                                                 | -                |       |                                 |                                                      |
| [18] | Graphite rod            | Platinum          | 15                 | 0.1 M Oxalic acid + 0.05 Na$_2$SO$_4$            | -                |       | SEM, TEM, RAMAN, FTIR, XRD     | GO                                                   |
| [42] | Glassy Carbon Electrode | Platinum          | 0.01               | 0.1 M Phosphate Buffer Solution                  | -                |       | SEM, XRD, RAMAN, CV, DPV       | (RGO)/cobalt oxide (Co$_3$O$_4$) nanocomposite       |
|      |                         |                   |                    |                                                 | -                |       |                                 |                                                      |
| [43] | Carbon Paste Electrode  | Platinum          | -0.2 to 0.9        | 0.01 M orthoaminophenol + 0.5M HClO$_3$ + 0.1M LiCO$_3$ + 0.005M SDS | -                | 25 ± 2 | SEM                             | Magnetic functional graphene oxide (MFGO)             |
|      |                         |                   |                    |                                                 | -                |       |                                 |                                                      |
| [32] | Flexible graphite foil  | Platinum          | 1 to 2             | 98 wt% H$_2$SO$_4$                               | 10 to 30 minutes | 25 ± 2 | GC-MS, SEM, TEM, FT-IR, XRD, RAMAN, AFM | GO Powder                                          |
Table 1: Summary of operational condition of electrochemical synthesis of graphene based material using platinum as the counter electrode (cont.)

| Ref | Working electrode | Counter Electrode | Power supplies (V) | Electrolyte | Exfoliation time | T (℃) | Characterization analyses | Type of graphene based material |
|-----|-------------------|-------------------|--------------------|-------------|------------------|-------|--------------------------|--------------------------------|
| [44] | Graphite          | Platinum          | 10                 | H₂SO₄       | 4 hours          | -     | XRD, FT-IR, SEM, 13C-NMR | GO sheets                      |
| [45] | Glassy Carbon Electrode | Platinum     | -0.3 to 0.6        | -           | -                | -     | SEM, TEM                | Polypyrrole (PPy), reduced graphene oxide (RGO), and gold nanoparticles (nanoAu) biocomposite |
|     |                   |                   |                    |             |                  |       | RAMAN, XPS, SEM, AFM/SKPFM | Reduced graphene oxide (rGO)/copper (Cu) composite films |
| [46] | GO sample         | Platinum          | 0.6                | -           | -                | -     | RAMAN, XPS, SEM, AFM/SKPFM | Reduced graphene oxide and poly(m-aminobenzenesulfonic acid, ABSA) nanocomposite (PABSA–rGNO) |
|     |                   |                   |                    |             |                  |       | SEM, TEM, FT-IR, XRD    | Graphene quantum dots from graphene oxide |
| [48] | Glassy Carbon Electrode | Platinum   | -                  | Propylene Carbonate with LiClO₄ | -    | FESEM, HRTEM, AFM, CV     | Graphene quantum dots from graphene oxide |
| [33] | Graphite          | Platinum          | 3                  | 0.1M H₂SO₄   | 4 hours          | -     | RAMAN, FTIR, EIS, CV     | GO                                |
| [49] | Glassy Carbon Electrode | Platinum    | -0.8 - +1.4        | CTAB + 0.1M H₂SO₄ | -   | FESEM, EDX, FTIR, XRD     | Poly(CTAB)/GO                       |
| [50] | Graphite          | Platinum          | H₂SO₄              | -           | -                | -     | SEM, FTIR, XRD, TGA, DSC | Multilayer GO                     |

"-": Data was unavailable
Figure 1: Frequency distribution of characterization analyses of the graphene-based material (GO/rGO) based on the curated articles in Table 1.
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References

1. Pei, S. and H.-M. Cheng, *The reduction of graphene oxide*. Carbon, 2012. 50(9): p. 3210-3228.
2. Sadegh, H., *Development of graphene oxide from graphite: a review on synthesis, characterization and its application in wastewater treatment*. Reviews on Advanced Materials Science, 2017. 49(1).
3. Kumar, H., et al., *Recent advancement made in the field of reduced graphene oxide-based nanocomposites used in the energy storage devices: A review*. Journal of Energy Storage, 2021. 33: p. 102032.
4. Marcano, D.C., et al., *Improved synthesis of graphene oxide*. ACS Nano, 2010. 4(8): p. 4806-14.
5. Zhou, Q., Y. Lu, and H. Xu, *High-yield production of high-quality graphene by novel electrochemical exfoliation at air-electrolyte interface*. Materials Letters, 2019. 235: p. 153-156.
6. Siaw, W.C., et al., *Synthesis of graphene oxide from industrial waste*. IOP Conference Series: Materials Science and Engineering, 2020. 778: p. 012050.
7. Ryu, B.D., et al., *Gallium dopant-induced tunable electrical properties of reduced graphene oxide using metal organic chemical vapor deposition*. Applied Surface Science, 2020. 504: p. 144500.
8. Mehravar, S., S. Fatemi, and M. Komiyama, *Magnetic property and structural study of nickel supported on reduced graphene oxide prepared by chemical vapor deposition*. Surface and Interface Analysis, 2020.
9. Xie, X., Y. Zhou, and K. Huang, *Advances in Microwave-Assisted Production of Reduced Graphene Oxide*. Frontiers in Chemistry, 2019. 7(355).
10. Yang, B., et al., *Synthesis of graphene by microwave irradiation for dye adsorption*. RSC Advances, 2014. 4(110): p. 64771-64780.
11. Wang, X., et al., *Fast and facile microwave-assisted synthesis of graphene oxide nanosheets*. RSC Advances, 2014. 4(104): p. 60102-60105.
12. Achee, T.C., et al., *High-yield scalable graphene nanosheet production from compressed graphite using electrochemical exfoliation*. Scientific reports, 2018. 8(1): p. 1-8.
13. Liu, F., et al., *Synthesis of graphene materials by electrochemical exfoliation: Recent progress and future potential*. Carbon Energy, 2019. 1(2): p. 173-199.
14. Lee, X., et al., *Review on graphene and its derivatives: Synthesis methods and potential industrial implementation*. Journal of The Taiwan Institute of Chemical Engineers, 2019. 98: p. 163-180.
15. Li, L., et al., *Review—Progress of Research on the Preparation of Graphene Oxide via Electrochemical Approaches*. Journal of The Electrochemical Society, 2020. 167(15): p. 155519.
16. Sharif, F., et al., *Synthesis of a high-temperature stable electrochemically exfoliated graphene*. Carbon, 2020. 157: p. 681-692.
17. Chen, K., D. Xue, and S. Komarneni, *Nanoclay assisted electrochemical exfoliation of pencil core to high conductive graphene thin-film electrode*. Journal of colloid and interface science, 2017. 487: p. 156-161.
18. Chen, D., et al., *Photosynergetic Electrochemical Synthesis of Graphene Oxide*. Journal of the American Chemical Society, 2020. 142(14): p. 6516-6520.
19. Jibrael, R.I. and M.K.A. Mohammed, Production of graphene powder by electrochemical exfoliation of graphite electrodes immersed in aqueous solution. Optik, 2016. 127(16): p. 6384-6389.

20. Aghamohammadi, H., A. Heidarpour, and S. Ghasemi, Electrochemical synthesis of fluorinated graphene nanoplatelets in electrolytes containing hydrofluoric acid and TiO2 nanoparticles. FlatChem, 2020. 22: p. 100172.

21. Prakoso, B., et al., Facile synthesis of battery waste-derived graphene for transparent and conductive film application by an electrochemical exfoliation method. RSC Advances, 2020. 10(17): p. 10322-10328.

22. Wang, H., et al., Preparation of graphene sheets by electrochemical exfoliation of graphite in confined space and their application in transparent conductive films. ACS applied materials & interfaces, 2017. 9(39): p. 34456-34466.

23. Lowe, S.E., et al., The role of electrolyte acid concentration in the electrochemical exfoliation of graphite: Mechanism and synthesis of electrochemical graphene oxide. Nano Materials Science, 2019. 1(3): p. 215-223.

24. Sahoo, S.K., et al., Industrial scale synthesis of few-layer graphene nanosheets (FLGNS): an exploration of electrochemical exfoliation approach. Journal of Applied Electrochemistry, 2020. 50(6): p. 673-688.

25. Nurhafizah, M.D., et al., Effect of voltage applied for graphene oxide/latex nanocomposites produced via electrochemical exfoliation and its application as conductive electrodes. Diamond and Related Materials, 2020. 101: p. 107624.

26. Md Disa, N., et al., The Synthesis of Graphene Oxide via Electrochemical Exfoliation Method. Advanced Materials Research, 2015. 1109: p. 55-59.

27. Chernysheva, M.N., et al., Investigation of sulfuric acid intercalation into thermally expanded graphite in order to optimize the synthesis of electrochemical graphene oxide. Journal of Electroanalytical Chemistry, 2020. 858: p. 113774.

28. Shen, Y., et al., Structure and Properties Evolution of Graphene Oxide Sheets During Low-Temperature Reduction on a Solid Substrate. The Journal of Physical Chemistry C, 2020.

29. Cao, J., et al., Two-Step Electrochemical Intercalation and Oxidation of Graphite for the Mass Production of Graphene Oxide. Journal of the American Chemical Society, 2017. 139(48): p. 17446-17456.

30. Pei, S., et al., Green synthesis of graphene oxide by seconds timescale water electrolytic oxidation. Nature Communications, 2018. 9(1): p. 145.

31. Kumar, N. and V.C. Srivastava, Simple Synthesis of Large Graphene Oxide Sheets via Electrochemical Method Coupled with Oxidation Process. ACS Omega, 2018. 3(8): p. 10233-10242.

32. Díez-Pascual, A.M., et al., Tailorable synthesis of highly oxidized graphene oxides via an environmentally-friendly electrochemical process. Nanomaterials, 2020. 10(2): p. 239.

33. Konwar, S., et al., High Purity Graphene Oxide Using Electrochemical Synthesis and Its Application in Macromolecular Symposia. 2019. Wiley Online Library.

34. Gao, Z., et al., Electrochemical synthesis of layer-by-layer reduced graphene oxide sheets/polyaniline nanofibers composite and its electrochemical performance. Electrochimica Acta, 2013. 91: p. 185-194.

35. Díez-Pascual, A.M., et al., Determination of riboflavin based on fluorescence quenching by graphene dispersions in polyethylene glycol. RSC Advances, 2016. 6(24): p. 19686-19699.

36. Li, S.-J., et al., Electrochemical synthesis of a graphene sheet and gold nanoparticle-based nanocomposite, and its application to amperometric sensing of dopamine. Microchimica Acta, 2012. 177(3): p. 325-331.

37. Tuinstra, F. and J.L. Koenig, Raman spectrum of graphite. The Journal of chemical physics, 1970. 53(3): p. 1126-1130.
38. Shen, Y., et al., Structure and Property Evolution of Graphene Oxide Sheets during Low-Temperature Reduction on a Solid Substrate. The Journal of Physical Chemistry C, 2020. 124(26): p. 14371-14379.
39. Nishina, Y. and S. Eigler, Chemical and electrochemical synthesis of graphene oxide – a generalized view. Nanoscale, 2020. 12(24): p. 12731-12740.
40. Razmi, H., L. Ezzati, and Z. Khorablou, Direct Electrochemical Synthesis of Graphene Oxide/Cobalt Oxide Nanocomposite on Pencil Graphite Electrode for Highly Sensitive and Selective Detection of Insulin in Pharmaceutical Samples. Journal of The Electrochemical Society, 2019. 166(12): p. B961-B968.
41. Martin, A., et al., Template Electrolysis of High-Performance Graphene Microengines. Small, 2015. 11(29): p. 3568-3574.
42. Dinesh, B., et al., In situ electrochemical synthesis of reduced graphene oxide-cobalt oxide nanocomposite modified electrode for selective sensing of depression biomarker in the presence of ascorbic acid and dopamine. Journal of Electroanalytical Chemistry, 2017. 786: p. 169-176.
43. Ehsani, A., et al., Electrolysis, physioelectrochemical and theoretical investigation of poly ortho aminophenol/magnetic functional graphene oxide nanocomposites as novel and hybrid electrodes for highly capacitive pseudocapacitors. Journal of Colloid and Interface Science, 2017. 490: p. 695-702.
44. Singh, P.K., et al., Electrochemical synthesis of graphene oxide and its application as counter electrode in dye sensitized solar cell. Journal of Renewable and Sustainable Energy, 2014. 6(1): p. 013125.
45. Wu, B., et al., Electrochemical synthesis of polypyrrole, reduced graphene oxide, and gold nanoparticles composite and its application to hydrogen peroxide biosensor. Nanomaterials, 2016. 6(11): p. 220.
46. Xie, G., M. Forslund, and J. Pan, Direct electrochemical synthesis of reduced graphene oxide (rGO)/copper composite films and their electrical/electroactive properties. ACS Applied Materials & Interfaces, 2014. 6(10): p. 7444-7455.
47. Yang, T., et al., Direct and freely switchable detection of target genes engineered by reduced graphene oxide-poly (m-aminobenzenesulfonic acid) nanocomposite via synchronous pulse electrolysis. Analytical chemistry, 2013. 85(3): p. 1358-1366.
48. Kalita, H., et al., Electrochemical synthesis of graphene quantum dots from graphene oxide at room temperature and its soil moisture sensing properties. Carbon, 2020.
49. Abraham, P., et al., Electrochemical synthesis of thin-layered graphene oxide-poly (CTAB) composite for detection of morphine. Journal of Applied Electrochemistry, 2020. 50(1): p. 41-50.
50. Yakovlev, A., et al., Electrochemical Synthesis of Multilayer Graphene Oxide by Anodic Oxidation of Disperse Graphite. Russian Journal of Electrochemistry, 2019. 55(12): p. 1196-1202.