Chapter

Electrochemical Exfoliation of 2D Advanced Carbon Derivatives

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Abstract

Advanced 2D carbon materials such as graphene and derivatives are basic building blocks for future nanostructured generation in electronics and energy horizons owing to their remarkable physical and chemical properties. In this context, production scalability of 2D materials having high purity with distinctive and multi-functionalities, that facilitate in fundamental research and advanced studies as well as in industrial applications. A variety of techniques have been employed to develop 2D advanced carbon materials, amongst state-of-the-art synthetic protocols, electrochemical is deliberated as a promising approach that provides high yield, great performance, low cost, and excellent up-scalability. Notably, playing with electrochemical parameters not only allows tunable properties but also enhances the content variety from graphene to a wide spectrum of 2D semiconductors. In this chapter, a succinct and comprehensive survey of recent progress in electrochemical exfoliation routes and presents the processing techniques, strategic design for exfoliations, mechanisms, and electrochemistry of graphene.

Keywords: 2D materials, electrochemistry, exfoliation, anodic exfoliation, cathodic exfoliation

1. Introduction

Two-dimensional (2D) materials motivated scientific society owing to inspired decisive passion in electrical, mechanical, and optical disciplines, showing extraordinary properties comparatively layered bulky counterpart. 2D pioneer carbon material, graphene, previously presented advanced studies in the fields, particularly, [1] membranes, [2] bio-sensors, [3] energy storage technologies, [4, 5] and topographic spintronics devices, [6] despite last decade advancement in graphene literature approach, still alarming goal from its targets, as is the condensed matter physics, [7, 8] towards the aforesaid trend, a series of ultrathin materials were isolated via exfoliation process, as synthesized incorporating metal chalcogenides, [9, 10] double-layered-hydroxide, [11] boron nitride, [12] preliminary investigation regarding 2D nano-materials was attractively oriented by fundamental research approaches inheriting novelty properties, new channels have certainly opened and encouraged recently towards high application inspired studies [13, 14]. Evidently, 2D materials frequently contributed active counterpart as a promising one in functional devices and versatile electronics. Eventually, they prove themselves as attracting candidates, revolutionizing the current technologies, further as, seawater desalination, quantum computing, and renewable energy resources [15–17].

Harvesting applications regarding 2D materials are expected to realize high efficiency with low-cost industrial-scale technologies should be appreciated in the development of high-quality 2D materials. Updates now reveal various top-down adopted methods, likewise, scotch-tape. Chemical and liquid-based exfoliation was followed, fabricating layered 2D materials successfully [18]. Recent investigations have shown remarkable information about top-down approach, regarding time-consuming, hazardous chemical nature, and more defects generation. Comparatively, epitaxial growth, and chemical vapor deposition (CVD), bottom-up approaches have considerable capability of fabricating ultrathin 2D materials containing large surface- area [19]. Nevertheless, aforesaid bottom-up methods are so complex that they show costly high temperature and pressure, rather, more need to transfer the 2D materials fabricated products from metal surface to targeted substrate, making difficult for controlling the synthesis process, and may incorporation of defects and impurities into the products. Electrochemical technologies are usually carried out under mild conditions, in comparison with, other synthesis technologies, as they proven convenient and controllable conditions [20, 21]. Electrochemical exfoliation, for the layered bulk-material, likewise, anodic-oxidation cationic-intercalation and cathodic-exfoliation, using liquid-electrolyte, applying potential driven structural expansion, is a potential method, exfoliating 2D materials in a remarkable novelty fashion [22, 23]. The electrochemical technique is also employed as a quick and controllable tool for lithium/non-lithium intercalations [15, 16, 24–31] and considered as an effective technique for exfoliating and/or intercalates layered carbon materials to single or multi-layered 2D nanosheets [32–35].

Electrochemical reactions occur on electrode with layered structure will yield as intercalation and/or exfoliation of electrode [36–38]. There are some desirable features for electrochemical exfoliation such as simplicity, fast cycle time, ease of activity, control, and potential for scaling up. The applied potential and electrolyte quality highly influenced on consistency of exfoliated nanosheets [39]. For this purpose, a set-up similar to the battery test system in a galvanostatic discharge mode with a constant current is used. In this context, a metallic lithium foil is used as anode and bulk Graphite powder is serves as cathode with $LiPF_6$ in a combination of ethylene carbonate and diethyl carbonate acting as electrolyte [16, 40]. Li^+ ions are introduced into graphene interlayer van der Waals gap during intercalation cycle and reduced by incoming electrons from the external circuit to Li atoms during insertion (**Figure 1**) [41]. Strongly in-plane covalently bonded bulk materials with weakly out-of-plane bonds, coupled by weak intermolecular forces, may easily be exfoliated in the form of thin-atomic layered structure of the 2D materials, by breaking weak van der Waals interactions under ultra-high cationic or anionic media [42, 43].

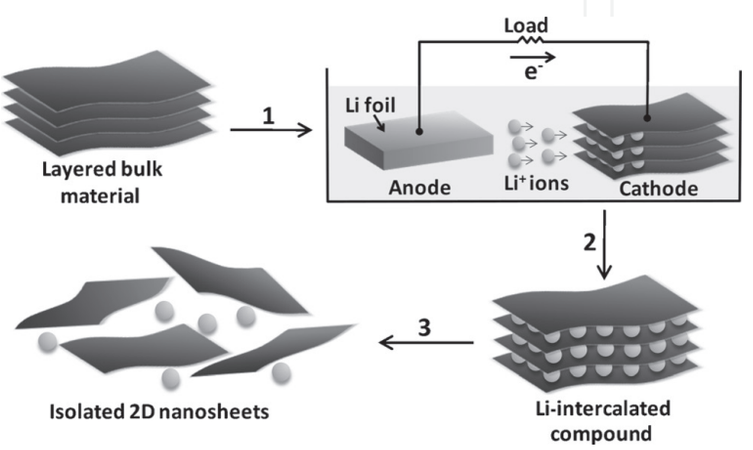

Figure 1.
Schematic illustration of electrochemical exfoliation [42].

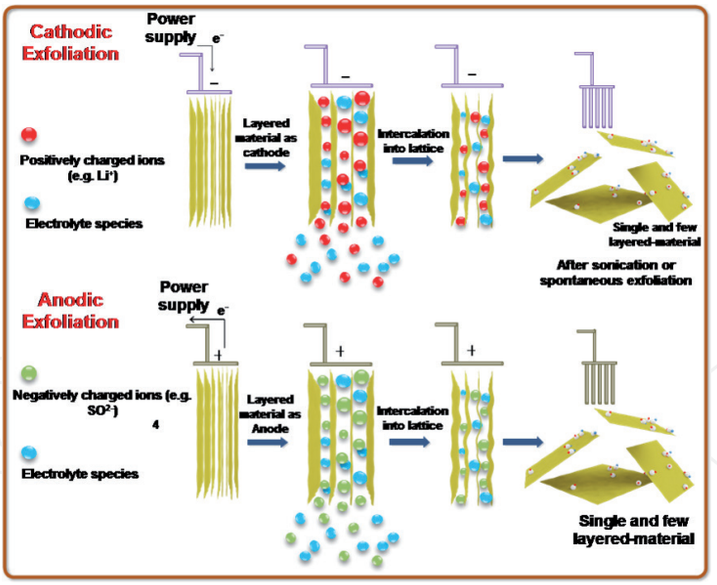

Figure 2.
Illustration of cathodic and anodic exfoliations.

The desired oxygen content, defect density, electrical conductivity, and thickness associated with exfoliated 2D materials, to be tuned, may be adjusted through voltage/current electrochemical parameters. Both cationic and anionic exfoliation, also intercalations, have been applied schematically in the exfoliation process of the graphite itself [44, 45], phosphorous black [46, 47] iv A and vA group metals [48, 49], transition-metal-dichalcogenides [32, 50, 51], graphitic-carbon-nitride, transition-metal-oxide [52], metal–organic-framework sheets [53] and MXene [54]. Based upon the type of potential used; electrochemical processes are mainly divided into two forms one is **(i) cathodic exfoliation**, performed in organic solvents such as Dimethyl sulfoxide (DMSO) and propylene carbonate comprising alkylammonium/lithium salts as electrolyte [16, 44, 55–59]. Other is **(ii) anodic exfoliation**, processed in ionic liquid or water mixtures or acids aqueous solutions such as H_2SO_4, $HClO_4$, H_3PO_4, and $H_2C_2O_4$; both exfoliations are described in **Figure 2** [22, 60–62].

2. History prospective of graphite intercalation chemistry

Graphite intercalation chemistry [63, 64] paves historical background path for the graphene, produced by electrochemically roots, the first step involves, typically, intercalation of ions in this respect. Scientists and engineers studied graphite intercalation compounds (GICs) over many decades, but exfoliation study of GIC was intensively increased to produce graphene/graphene-derivatives via characterization of graphene, employed by Geim and Novoselov [65]. A briefly reviewed of pre-graphene era work has been described here, included with the latest electrochemically produced graphene. GICs are identified, as numerous graphitic molecules resided between basic graphene sheets.. The intercalating molecules may play donor role in the graphitic network, otherwise, accept electrons (acting as accepters) to form chemically ionic-bond with graphite. Contrarily, a ternary GIC possibility prevails in the form of co-intercalated, acceptors and donors as well. GICs have interestingly presented considerable research study, owing to improved charming (electrical and electronic) properties relative to pure graphite. The very first reported literature on GIC was presented by Schafhäutl, in 1841 [66]. While, Various GICs methods have been promoted, producing the material under study, likewise, chemical photochemical and electrochemical synthetic approaches.

In addition, a homogeneous series of intercalating molecules were involved in various graphitic nature host materials [67], fabricating various GICs. GICs (amongst many species), including halogens, metal halides, alkali metals, and various acidic nature compounds are successfully incorporated into graphite. Electrochemical-intercalation-approaches have been studied since 1938, as Rüdorff and Hoffman employed electro-intercalation, to prepare acidic nature GICs [68]. However, until 1970s and 1980s, no interest has been taken in intensified electrochemically produced GICs. Moreover, in 1974, the Lithium/(CF) primary battery has been introduced by Fukuda while the 1970s presented the first lithium/graphite/fluoride battery-system on commercial basis, successfully [69, 70]. While electrochemical-intercalation approach was employed, here, a voltage is applied to graphitic working-electrode. In case the potential becomes positive, the graphite is identified as positively-charged anode, attracting anionic intercalating-species. In contrast, if the potential is opposite, then graphite acts as a negatively-charged cathode, which attracts cationic nature species. As a result, accordingly, both anionic-cationic intercalating-agents may be involved in the desired GICs. An anionic intercalating-species, which have been successfully incorporated, contained obviously sulfate- anions, fluoride-anions [71–73], and metal-halides respectively [74].

Cationic intercalating-species, including metals such as magnesium [34] and lithium have been reported [75, 76]. Lithium-ion GICs successfully exemplify the application of GICs towards the production of batteries, an area, where maximum research has been reproduced. GICs proved to be a successful battery cathode, or anode, or both alternatively. In the 1980s, lithium-ion GICs were progressed as anode-materials in secondary-batteries, associated with metal-oxide cathodes. Research into lithium-ion batteries progressively continues, currently, with due widespread commercial use this economical system. Furthermore, alternative GICs battery systems, such as metal-hydroxide-based systems [77], have also been adopted advanced steps and exhibited commercial based success. Various early electrochemically synthesized GICs products, based on the contemporary electrochemical-products of exfoliated-graphene and functionalized-graphene, i.e. early work on lithium/GICs advanced materials, which would be exfoliated to graphene, later on, were also appreciated [78]. Stage-I, earlier GIC literature on GICs, is considered the most relevant current-work on graphene exfoliation approach. As far as Stage I is concerned, compound is formed during the process of one layer of graphene resided between every layer of intercalating-molecules, whereas Stage-II GIC shows two-layers of graphene intercalated between each layer of guest-molecules. Stage-III GIC contains three-layered groups of graphene residing guest molecules, and continue simultaneously. Since Stage-I GICs, the guest species, enlarge the inter-layer spacing between graphene layers, following basic principle, each layer may easily be separated from its neighbor one, so becoming able to be exfoliated into single-layered graphitic nature. Much electrochemical-graphene work, decisively first creates Stage-I GICs, which are, later on, exfoliated in the form of monolayers. Earlier study reveals that electrochemically produced Stage-I GICs have been announced more informative in many studies, clearly described in the forthcoming sections. It is very likely, and innovatively, that this literature study will continue to be made a foundation for future work, successfully [79].

3. Electrochemical setup and exfoliation mechanisms

3.1 Experimental setup

The electrochemical setup, used for graphene exfoliation, usually incorporates the elements such as graphite working-electrode, counter-electrode,

reference-electrode, electrolyte, and voltage-supply. Systematically, highly-orientated pyrolytic-graphite (HOPG), graphite-powders, graphite-rods, graphite-foil, or graphite-flakes has been used as the working-electrode [22, 44, 80]. To provide the conducting surface, graphite flakes were choosed as the best, amongst available electrodes, that may be adhered to conductive carbon-tapes, forming the working-electrode [22, 45], and they may also adhere to tungsten-wire via silver-pad [81] or to be formed into graphite-plates through compression directly [82]. Being counter electrodes mesh, platinum-wire, plates or rods, and graphite were more frequently used. The arranged experimental setup is often illustrated as depicted in **Figure 3a**. Keeping a certain distance between working and counter electrodes respectively, they are simultaneously immersed into electrolyte. A voltage (positive or negative) is applied to the graphite (a working electrode), depending upon adopted desired exfoliation mechanism.

In addition to the aforesaid common setup, Liu et al. employed two pencil cores, as graphitic anode and cathode sources alternatively [80]. An alternating bias-voltage (between +7 V and − 7 V) was applied across the ends of pencil-electrodes, exfoliating them properly. Though the setup was highly efficient with higher exfoliation rate than graphite electrode, yet the product so obtained may be expected more inhomogeneous, with wide thickness and suitable size distribution. Abdelkader et al. reported, recently, a versatile setup in **Figure 3b**, showing continuous electrochemical-exfoliation-process, producing 0.5–2 g (few-layer graphene) per hour [83]. Moreover, in the setup, the graphitic electrode was injected steadily from the bottom of the electrolytic cell with graphitic contact with the electrolyte, being so exfoliated. Well- immersed-exfoliated (few-layer graphene sheets) was located on upper surface of the electrolyte, thereby, flowed out of the cell, while the partially-exfoliated-graphite retained at the bottom, so that further exfoliation may be carried out [83]. In another study, Motta and coworkers have presented ultra-sonication, assisting the electrochemical-exfoliation process, and placing the graphite electrode in a sonicated-exfoliated process [84].

Sorokina et al. introduced a patent experimental setup, comparatively, producing GICs in the past of the graphene era indicating a load (20 kPa) was applied across graphite-flakes over a platinum-disk (electrode), so to achieve fine electrical-contacts between the graphite-flakes as well [85]. Recently, the main challenging issue lies between (the effective and uninterrupted) electrical-delivery, to each graphene layer, in the graphite, presenting the immense need for the development of commercially scalable, and further controllable-setup.

3.2 Electrode preparation

Various bulk-layered materials exhibit strong in-plane bonds while electrostatic interactions with weak interlayer bonding i.e., interlayer-cohesive-energies (less than 200 meV/atom) [18]. So, exfoliation or delamination occurred in the form of atomically thin-layered nanosheets, thereby, van der Waals forces amongst 2D binding layers reduce to a minimum level. Mechanical exfoliation/chemical exfoliation as compared with ultrasonic treated exfoliation was extensively carried out fallowed by two-electrode or three-electrode electrolysis of electrochemical exfoliation (using bulk-material as working-electrode). Plasma state as well as cations or anions accumulated between layers owing to a strong electric field, resulting in layered-structure electrodes expansion with the interlayer-bonding cleavage simultaneously. Hence, bulk-layered-structured material may prove to be a good conductor of electricity, thereby, could be made electrode. It has been reported that bulk layered materials are semiconductive as well as non-conductive in nature [86] caused by difficult to be electrochemically exfoliated, as in this case, the most applied potential causes overwhelming large resistance. To overcome issue, a

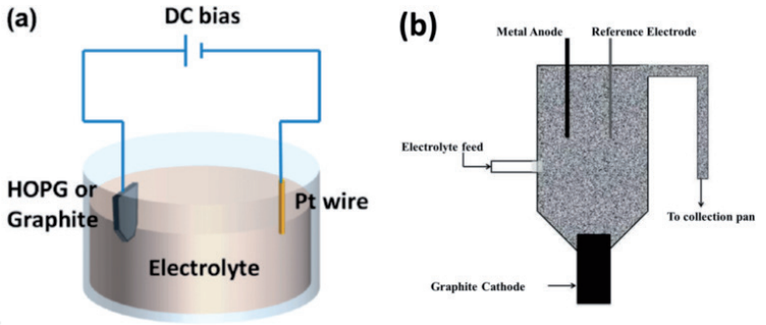

Figure 3.
(a) Schematic illustration of a typical setup for electrochemical exfoliation of graphite [81], (b) schematic of the electrochemical cell for continuous process [83].

conductive additive is suggested to be more appropriate strategy [61], resulting in exfoliation of 2D layered materials in an extensive range of possibility while ignoring conductivity of the bulked layered materials.

During the exfoliation mechanism, expansion of bulk material electrode occurs under the intercalation of ions, leading to disintegration of bulk material electrodes. Resultantly, some disintegrated sheets were still not exfoliated, reducing the yield strength and preventing electrochemical exfoliation process from the possibility of feasible production route. During the intercalation process, chances of breaking of bulk material electrodes, they are wrapped up in confined space with plastic tube and platinum gauze or carbon cloth, suggesting reasonable method for laboratory preparation method [87, 88]. Currently, Achee et al. framed a new route, yielding highly scalable 2D graphene by employing graphite flakes, without binder as the working electrode [89]. Graphite flakes remained in electrical contact under the compressed expandable electrode system, expanded by gas evolution. Therefore, graphene powders accumulated continuously expanded largely, and exfoliated extensively to produce carbon materials (graphene), 2D in nature.

3.3 Electrochemistry of exfoliated graphene and mechanism

The electrochemical exfoliation Mechanism depends on the type of applied potentials (anodic or Cathodic, **Figure 4**). Amongst the going mechanisms, anodic-exfoliation contains an anionic-intercalation with any co-intercalating-species (in the reaction mixture) into graphitic nature material. A positive current extracts electrons from the graphite (a working anode), thereby producing a positive charge. The charge, so produced, proceeds of bulky negative ion's intercalation like sulfate anions, that have increased the interlayer-spacing between graphene-sheets, and further supported during the exfoliation of the sheets, subsequently. A negative biased graphitic working-electrode in cathodic exfoliation attracts positively-charged-ions (e.g. Li^+) in the electrolytic solution, involving any co-intercalating molecules. Furthermore, the intercalating species create a location where they open the graphene sheets, depending upon expansion and exfoliation processes [16, 90, 91].

After completion of electrochemical intercalation along with expansion of graphite, further need is required to some form of exfoliation. In some cases, where exfoliation-process may occur during which intercalates (more typically), or the co-intercalating species, such as water, that was rapidly transformed to expanded-species (e.g. oxygen gas) [81]. On the other hand, electrochemically expanded graphitic sheets requires, to be mechanically-exfoliated likewise sonication process [78]. The exact mechanism related to electrochemical-graphene-exfoliation

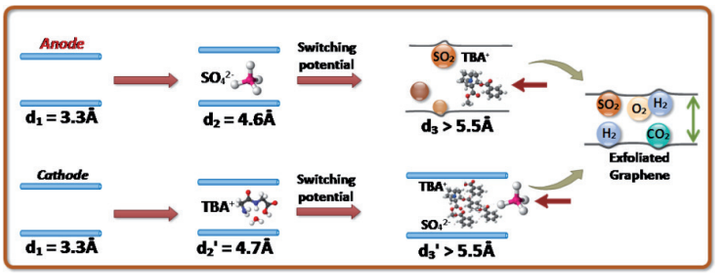

Figure 4.
Proposed mechanism for exfoliation process at both anode and cathode.

depends upon the potential polarity, along with other experimental conditions, caused by the electrolyte as well as co-intercalating agents already incorporated in the mechanism, to be further discussable (vide infra) [15].

An anodic exfoliation mechanism in ammonium sulfate ($(NH_4)_2SO_4$) aqueous solution, outlined by Parvez et al. [22]. In (**Figure 5a**), Hydroxyl ions (OH^-), firstly produced from the water electrolysis, and this strong nucleophile may interact the sp^2 carbons graphitic- edges with grain boundaries, thus producing two vicinal hydroxyls (OH) groups. Subsequently, they interact with each other, exploring epoxide group rings. Alternatively, dissociating them forming of two carbonyl-groups via further additional oxidation, as illustrated in **Figure 5b**, reaction (3). Resultantly, this leads to depolarization with an expansion of graphitic-layers at the corners, which in turn opened up the lattice, for intercalation, by sulfate ions SO_4^{2-}, providing opportunity towards possibly more water molecules. In addition, along with the oxidation of graphite, further reactions are certainly expected to occur, such as involvement of evolution of (CO_2 and O_2 gases respectively) by performing reactions 4 and 5 in **Figure 5**. CO_2 and O_2 gases also assisted reasonably during the exfoliation of the graphitic layers [22].

Similarly, anodic process was also described by Rao et al. [92]. Hydroxyl ions (i.e. OH^- ions) from aqueous NaOH electrolytic solution reacted with more added H_2O_2 to form O_2^{2-} ions that have proved to be more nucleophile than OH^- ions. That is why, they may be easily intercalated into graphene-sheets, with the aid of (a positive) electrochemical-potential. As an example of a cathodic exfoliation mechanism, Li^+ (positive ions) in organic solvent PC (propylene carbonate) may be systematically used as intercalating-agents [44, 78]. Electrochemical process was achieved by the co-intercalation of PC and Li^+ ions in the form of negatively charged graphitic layers, as illustrated in **Figure 6**.

By supplying sufficiently high voltage, the organic solvent will be decomposed, producing propylene gas which added the graphitic expansion [44].

Alkaline situations along with 1 M of sodium hydroxide (NaOH) and father explore the impact of adding hydrogen peroxide (H_2O_2) on exfoliation efficacy, experimental setup with mechanism as shown in **Figure 7a, bi-ii**. The existence of H_2O_2 considerably improves the exfoliation due to formation of extremely nucleophilic ions (O_2^{2-}) that causes to intercalate and magnify graphene layers. This corresponds to the extremely reactive radicals (i.e. O and OH) produced by firstly, anodic oxidation of water and secondly, opened and oxidized the edge sheets assisting intercalations of the peroxide ions **(Figure 7f-g)**. The exfoliation route happens tremendously fast and obtained graphene sheets attaining a low density of defects and low oxygen group content **(Figure 7c-e)**. Further, exfoliation approaches for graphite using anodic mechanism were projected using phosphate, nitrate, carboxylate, and perchloride [16, 93]. Likewise, Abdelkader et al. used Li^+ and alkylammonium ions (Et_3NH^+), in dimethyl sulfoxide (DMSO), intercalating into graphitic-layers, while weakening the van der Waals interactions between the

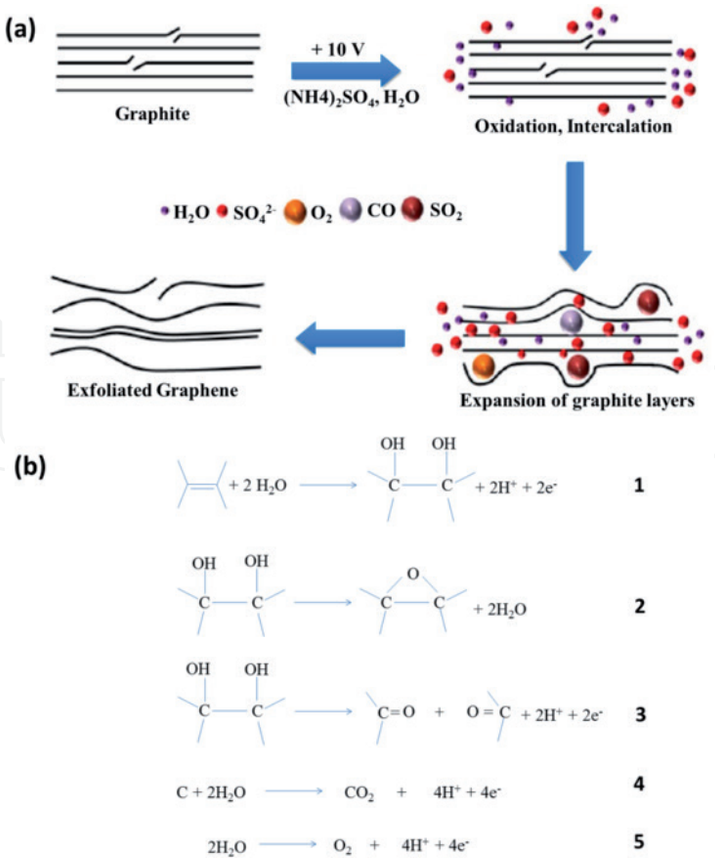

Figure 5.
(a) Schematic illustration of mechanism of electrochemical exfoliation in $(NH_4)_2SO_4$ aqueous solution [22], (b) electrochemical oxidation reactions occurs at anode for graphite exfoliation [56].

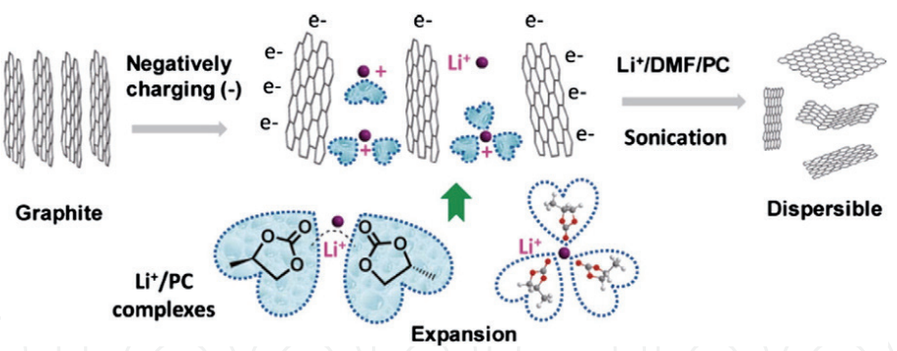

Figure 6.
Exfoliation of graphite into few-layer graphene flakes via intercalation of Li^+ complexes [44].

layers [83]. Simultaneously, Et_3NH^+ was likely reduced electrochemically to Et_3N gas, supported by graphitic exfoliation successfully.

3.4 Anodic exfoliation

Amongst many electrochemical exfoliation methods, anodic graphite exfoliation is that one, showing high exfoliation efficiency. Various diversified graphene production approaches were adopted, based on anodic exfoliation, which has already been reported [22, 60, 94–96]. Su et al. presented the best one approach (as the first reported) of anodic exfoliation, via adopting the most simple and fast method, while preparing electrolyte solution containing H_2SO_4 + KOH [81]. An optimized procedure that was followed here, for the exfoliated graphene production was the setup, similar to what is shown in **Figure 3a**, using the electrolyte with value (pH = 1.2). A low-biased +2.5 V has been first applied for 1 min, yet with

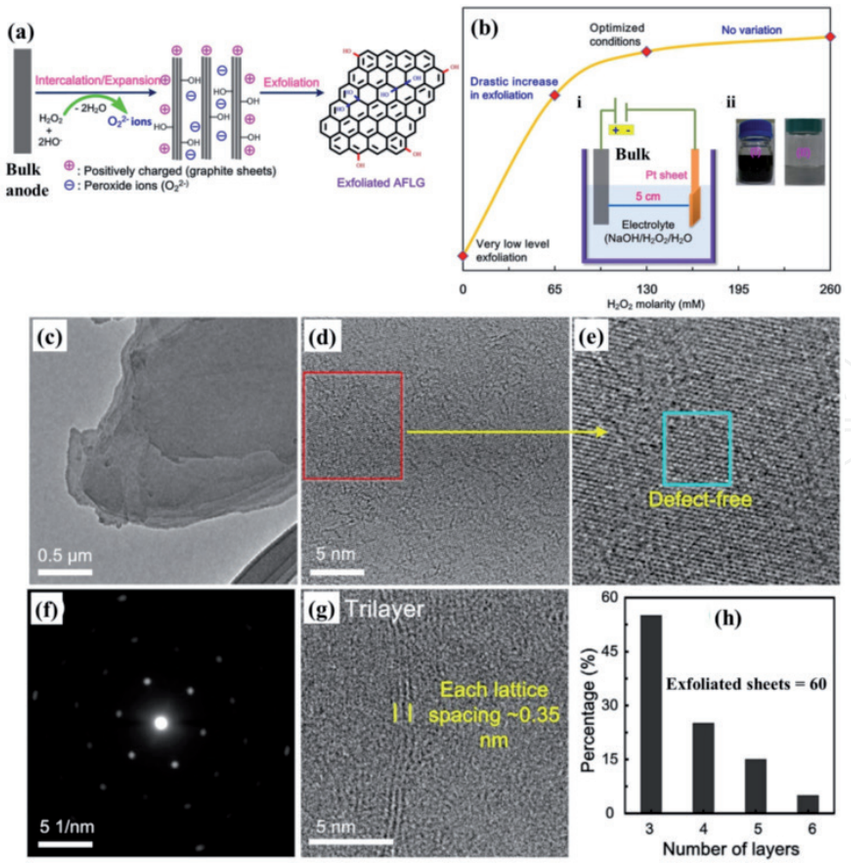

Figure 7.
(a) Schematics of proposed mechanism of anodic exfoliation (bi, ii) experimental setup and exfoliation efficiency against H_2O_2 molarity with photograph of dispersed nanosheets in C_3H_7NO. (c, and d) low magnification (0.5 μm) and HR-TEM images of exfoliated nanosheets, respectively, (e) image reveals some defects in nanosheets (f) SAED image (g) HR-TEM image, exposing tri-layer formation, (h) distribution of exfoliated nanosheets before centrifugation [92].

subsequent alternating-voltage between +10 V and − 10 V. In first step, low-voltage, aided for forming the wetting electrode surface, helping intercalation of anions into the graphite. Subsequently, the +10 V potential was used, for activating and oxidizing the graphitic sheets, which caused the graphite to become quickly in the form of dissociated small pieces. The ensuing (−10 V) potential was used as reductants towards functional groups. Very impressively, the so produced graphene sheets show a lateral size of several to 30 μm. Above 60% of the sheets were observed as bilayer-graphene with A–B stacking as illustrated in (**Figure 8**). Oxygen functional groups along with some decisive defects have been detected in the graphene sheets attributing to unavoidable oxidation. Moreover, the concentration level of graphitic defects produced in graphene sheets was less than reduced graphene oxide, which was produced by traditional chemical methods.

A similar study was presented by Su and colleagues [81], showing optimized multiple parameters, involving pH as well as applied voltage. While at extremely low pH, with high oxidation levels including H_2SO_4, produced a maximum level of defects on the graphene sheets. Consequently, KOH was added along with H_2SO_4, to increasing the pH value of the electrolyte, exhibiting the exfoliation at lower rate. Resultantly, it was observed that higher concentrated pH showed large percentage of bilayer-sheets, but the non-uniform defect level was still maintained between the graphene sheets. Subsequently, at less than 10 V potential (in terms of the working biased potential), the exfoliation process was slowed down and more inefficient, whereas voltages (greater than 10 V) accelerated the exfoliation rate very fast so that density of graphitic-particles, as well as, thickest graphene sheets were clearly observed and largely produced. Obviously, the effects of various electrolytic

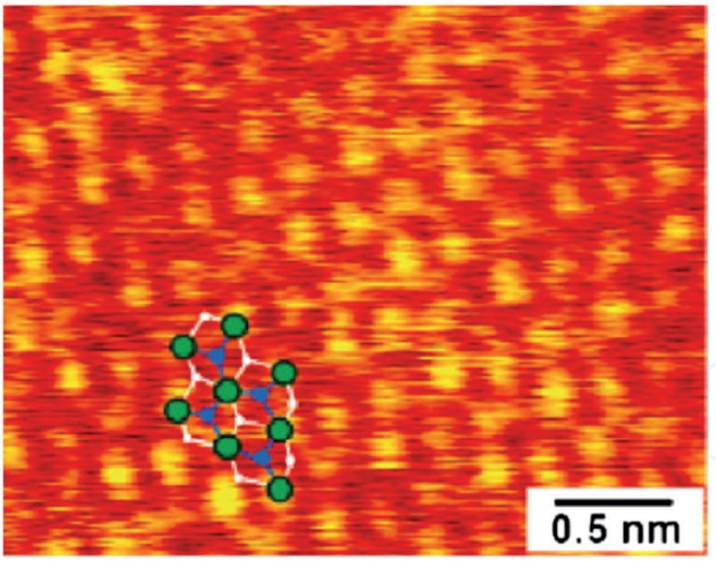

Figure 8.
STM image of bilayer graphene produced by Su et al. hexagons represent atom configuration of two layers [81].

solutions were greatly explored, involving some acids, such as HBr, HNO_3, HCl, and H_2SO_4, however, amongst the aforesaid solutions, H_2SO_4 was found only to be more effective in the performed experiments.

In 2013, Parvez et al. contributed and demonstrated their work in the form of exfoliation process of graphite in H_2SO_4 aqueous solution, further proceeding and elucidating, the exfoliation mechanism as well [45]. In this respected end, they have been explored the influence of H_2SO_4 concentration more clearly on exfoliation performance, by using (+10 V voltage), for 2 minutes subsequently. It was, more certainly, found that 1 M and 5 M H_2SO_4 explored slow exfoliation efficiency and yielded 0.1 M H_2SO_4, presumably, because of (more concentrated H_2SO_4 solutions), generated larger fragments of graphitic-particles. Likewise, in case of sulfuric acid, was too low, the exfoliation efficiency was more frequently reduced, caused by a reduced number of anions. The worthy authors have deeply studied while examining pure H_2SO_4 with 1:1 H_2SO_4/CH_3COOH reaction mixture, however, in these cases, slight expansion with almost no exfoliation was prominently observed so far. This scheme has suggested the durability of water in the electrochemical process, as it clearly may produce (oxygen and hydroxyl radicals), which arises as aiding agents in intercalation and exfoliation processes. High-quality graphene was exfoliated via 0.1 M sulfuric acid solution, with a large sheet, containing a size of ~10 μm, with low oxygen concentration 7.5 wt.% along with low sheet-resistance (of 4.8 kΩ/square), for a single sheet as in **Figure 9a**-**f**.

Liu et al. presented electrochemically exfoliation of two graphitic-electrodes, through applied alternating potentials (+7 V and − 7 V) in aqueous electrolytes, containing H_2SO_4 or H_3PO_4, thereby, resulting in anodic-exfoliation using both electrodes alternately [80]. Depending upon Characterization results, graphene flakes with thick multilayered structure (3–9 nm), lateral size (1–5 μm) with comparatively low oxidation level, were produced (see **Figure 10**).

Xia et al. keenly observed, the swallowed and expanded graphitic surface, caused by the intercalation along with gas formation at early stage level [74]. Apparently, opening of graphitic edges is caused by a key-step towards the subsequent exfoliation. Furthermore, the radical attack was observed as nonselective, in this case, occurring randomly at the exposed graphitic surfaces, necessarily leading to increased oxidation level of the graphene sheets. Partial removal of the radicals indicates a sound solution, preventing the side reaction, so occurred. Yang

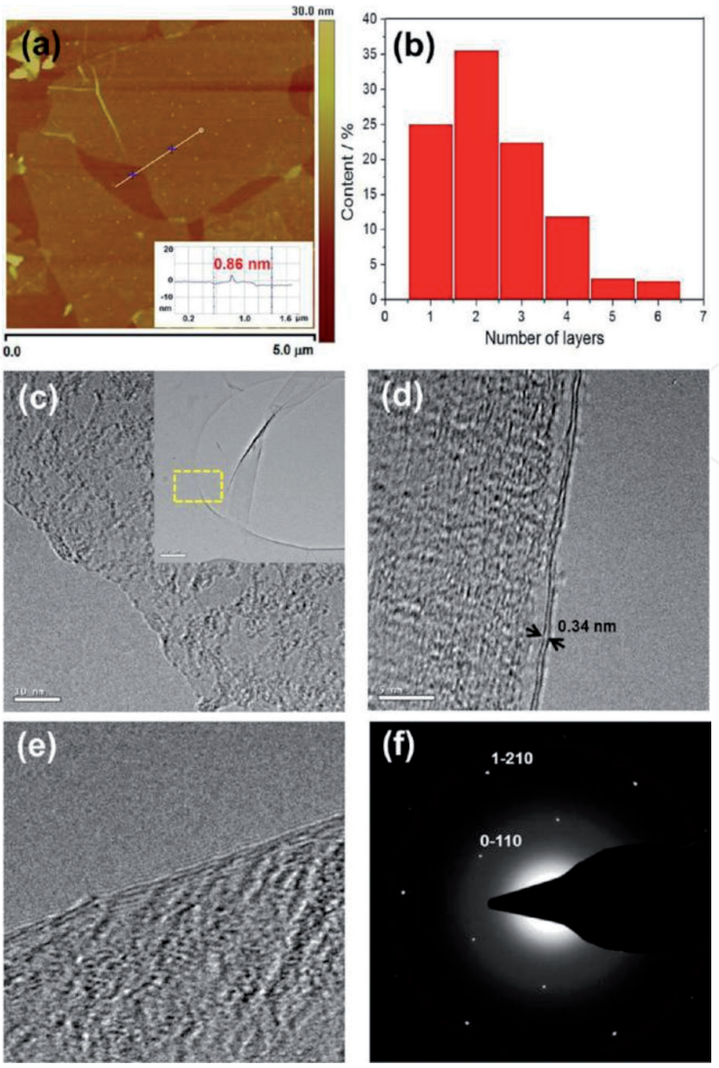

Figure 9.
(a) AFM image of electrochemically exfoliated graphene on substrate (SiO_2), (b) statistical thickness analysis of the graphene sheets by AFM, (c, d, and e) HR-TEM images of single-, bi-, and four-layer graphene; inset in (c) is the low magnification image of exfoliated graphene, and (f) SAED pattern of bilayer graphene [45].

et al. [97] have examined an antioxidants group, based on a standard ammonium sulfate $(NH_4)_2SO_4$ electrolyte, and with radical scavengers containing sodium borohydrides, ascorbic acid, (2,2,6,6,tetramethyl-piperidinyl)oxyl (TEMPO) acting as additives candidates during the exfoliation process. Consequently, the more addition of TEMPO causes greatly suppressed oxidation state, yet not compromised the exfoliation efficiency, with production of 15 g h^{-1} showing high quality graphene, exploring large dimensions (5–10 μm), but only few defects were observed in the form of C/O ratio equal to 25.3. **Figure 11** showed that TEMPO initially reacted with the ($HO^{\bullet}$ radicals) at anodic end, generating metastable TEMPOOH along with oxo-ammonium cations. At the Cathodic end, the aforesaid intermediates (compounds) were largely reduced to TEMPO radicals in again turn. In the system discussed here, single graphene sheets appeared to be an ultrahigh hole-mobility upto 405 $cm^2 V^{-1} s^{-1}$, owing to be still an excellent processibility in N,Ndimethylformamide (DMF) (6.0 mg mL^{-1}), preparing graphene ink as well.

3.5 Cathodic exfoliation

For decades, a graphitic negative electrode has been extensively used in lithium-ion battery-technology, owing to its high electrical conductivity and ability,

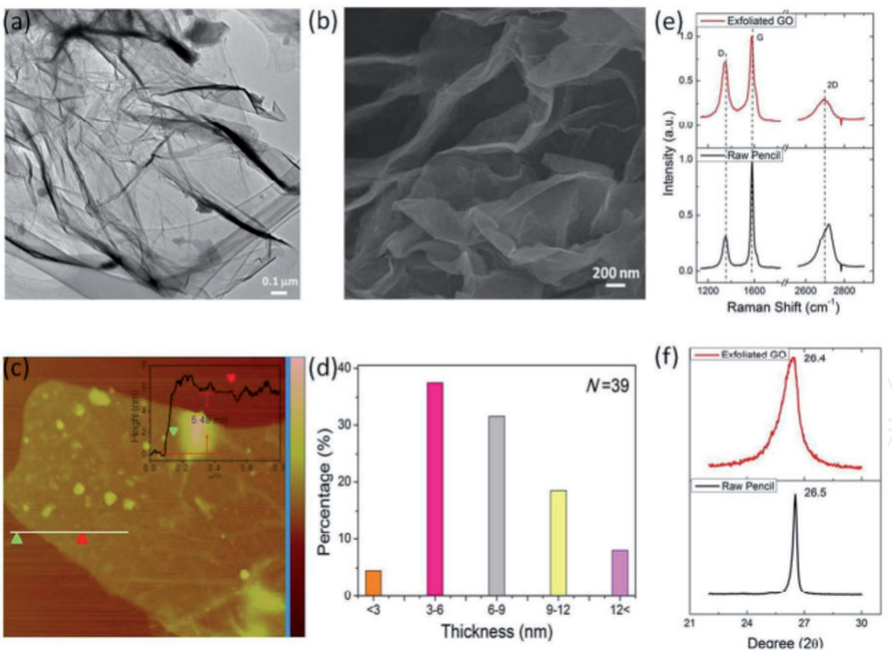

Figure 10.
(a) TEM image and (b) SEM image of exfoliated GO flakes, (c) AFM image of exfoliated GO flakes. The thickness is 5.45 nm with lateral size around 2 μm, (d) thickness distribution histograms for exfoliated GO sheets, as estimated from corresponding AFM analysis. The graphene flakes are mainly distributed in the range of 3–9 nm thickness (69%) with lateral size about 1 to few μm, (e) Raman spectra, and (f) XRD patterns for both pencil core and exfoliated GO flakes, respectively [80].

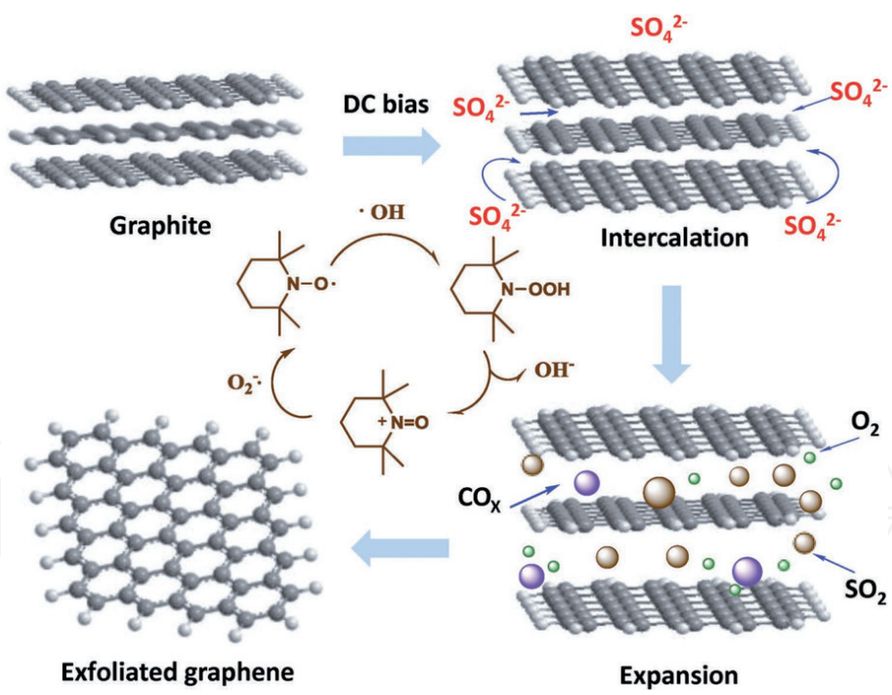

Figure 11.
Anodic exfoliation of graphite in an aqueous electrolyte with sulfate anions and TEMPO. TEMPO is a radical scavenger that partially eliminates the hydroxyl radicals from water oxidation [97].

for hosting lithium between the graphitic layers (**Figure 12**). In this way, the lithium-graphitic intercalation-compounds decomposed into water at a very fast rate, giving rise to lithium hydroxide along with free-standing graphene sheets. The aforesaid principle has been recently introduced, as a durable route towards scalable production of graphene [107]. However, depending on slow kinetics of the intercalation-process, the lithium was bounded to those areas closed to the edges. Upon exfoliation into water, graphitic expanded edges were clearly produced

Bulk materials	Electrolytes	Working potentials	Yield	Thickness	I_D/I_G	Ref.
HOPG/natural graphite	0.5 M H_2SO_4 + KOH (pH ≈ 1.2)	1) +2.5 V, 1 min; 2) Switching +10 V, 2 s; −10 V, 5 s	5–8 wt%	≤2 nm	0.5–1.0	[81]
Graphite foil	0.1 M H_2SO_4	+10 V, 10 min	60 wt%; 4.2 g h^{-1}	1–3 layers	0.4	[45]
Graphite foil	0.1 M $(NH_4)_2SO_4$	+10 V, 10 min	75 wt%; 16.3 g h^{-1}	1–3 layers	0.25	[22]
Graphite foil	0.05 M NaCl	+10 V, 60 min	—	2–3 nm	0.8	[98]
Expanded graphite foil	0.1 M NaOH + Na_2SO_4	1) +3 V, 3 min 2) +10 V, 30 min	—	2–3 nm	1.3	[99]
Expanded graphite foils	0.1 M $(NH_4)_2SO_4$ + 1 mg mL^{-1} TEMPO	+10 V, 10 min	75 wt%; 15.1 g h^{-1}	1–3 layers	0.1	[97]
Expanded graphite foil	0.5 M Na_2SO_4 + 0.05 M $CoSO_4$	+20 V, 120 min	—	Monolayer and few layers	0.05	[100]
Bulk graphite/ graphite powder	0.1 M H_2SO_4 + 1 mg mL^{-1} melamine	±20 V, 10 min	1.5 g h^{-1}	1–3 layers	<0.45	[101]
Graphite foil	0.2 M SNDS in water	+10 V, 60 min	—	2.5 nm	0.2	[36]
Graphite foil	30 mg mL^{-1} $LiClO_4$ in PC	−15 ± 5 V	>70 wt%; 0.12 g h^{-1}	<5 layers	<0.1	[44]
Graphite foils	0.1 M TBA HSO_4 + NaOH	±10 V, 0.1 Hz	75 wt%; 20 g h^{-1}	1–3 layers	0.15	[102]
Graphite foils	0.1 M $(NH_4)_2SO_4$ + 1% thiourea	±10 V, 0.1 Hz, 60 min	—	—	0.06–0.14	[103]
HOPG/graphite rod	0.1 M $(NH_4)_2SO_4$	switching +7 V or + 10 V, 1 s; −0.5 V, 3 s	77 wt%	<5 layers	0.29	[34]
Graphite foil	0.5 M $LiClO_4$ in water	1) +2.0 V, 2 min 2) +10 V	– (graphene oxide)	6–8 layers	1.0	[104]
Graphite flakes	1.0 M H_2SO_4 in saturated $(NH_4)_2SO_4$	anodic, 0.6 A, 24 h	40 wt% (graphene oxide)	1.5 nm	1.0	[55]
Graphite foil	1) 95% H_2SO_4 2) 0.1 m $(NH_4)_2SO_4$	1) +2.2 V, 10 min 2) +10 V	71 wt% (graphene oxide)	monolayers	1.48 ± 0.01	[105]
Graphite foil	1) 98% H_2SO_4 2) 50% H_2SO_4	1) +1.6 V, 20 min 2) +5 V	96 wt%; 12 g h^{-1}	1–3 layers	>1.0	[106]

Table 1.
A summary of electrochemical exfoliation and anodic oxidation of graphite.

and further intercalation also occurred positively, thereby, also water decomposition and sonication steps were necessarily taken, achieving complete exfoliation (**Figure 13**) [44]. Liu et al. and Huang et al. [108, 109] have presented much effort, for accelerating the intercalation kinetics, by using molten (LiOH or LiCl) at 600°C. However, the intercalation was considered there so insufficient to be achieved perfect graphitic exfoliation, but sonication steps thus fallowed were still required to achieve remarkable production of graphene-based materials.

Swager and Zhong [78] suggested a synergetic method to be intercalated the graphite primarily with Li^+, by following tetra-alkyl-ammonium cations into two steps separately. Moreover, due to expanded nature of the cathode, the distance between electrodes was kept initially very large, exploring the high potential difference required to apply, to dominate the high Ohmic-drop, created by the electrolytic cell configuration. Resultantly, the organic electrolytic solvent was dissociated in that state, occurring later on, at all the stages of the procedure by disappearing slowly during intercalation process. That is why, additional steps were rendered through sonication mechanism again, need to be sufficient for achieving reasonable exfoliation proceedings.

Dimethylsulfoxide (DMSO) has shown a wide electrochemical window that is highly efficient solvent during the graphene solvent dispersion, reflecting typical dispersive qualities, by comparing those of NMP [110]. As a result; DMSO forms various solvated ions, containing both lithium and alkylammonium ions reasonably. The observed solvated ions are expected to be able to intercalate with graphite, via decomposition between the graphene layers making SO_2 and/or along with amine-based apparent gases. The stress applied properly on the graphene sheets through the gaseous expulsion so occurred is evaluated enough to overcome the forces (van der Waals) that attracting the neighboring sheets, allowing separation of graphene sheets formed by the graphitic cathode, thereby, allowing dispersal occurring in the electrolytic solution. The authors of the literature [83] have applied the said principle to make many flakes, showing lateral dimension (upto 20 μm) of few-layer graphene towards DMSO-based electrolytic solution, containing triethylammonium and Lithium ions. Authors have adopted fashioned of electrochemical program, by applying a controlled Cathodic-potential towards the graphitic electrode, which presents complete intercalation prior to flakes formation spontaneously, so that exfoliation from the Cathodic end because of partial expansion occur consequently. It was greatly suggested that the triethylammonium ions, dissociated between the layers, give rise to triethylamine along with hydrogen gases, highly encouraging the exfoliation of flakes more prominently.

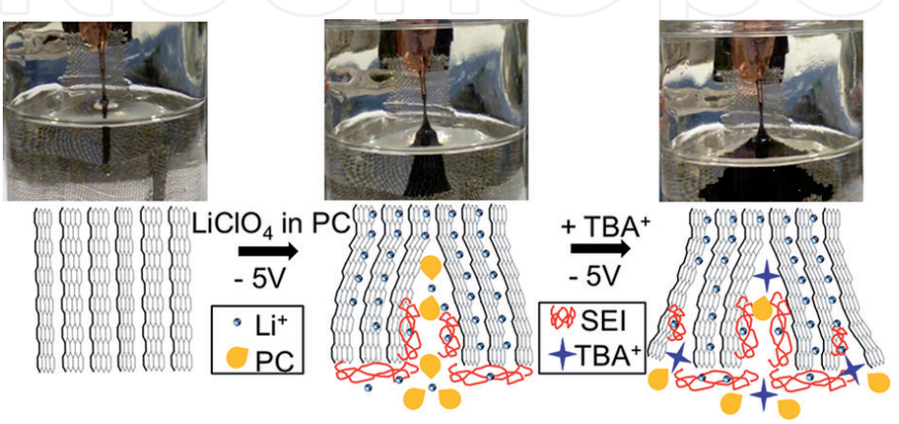

Figure 12.
Schematic and images of cathodic electrochemical expansion of graphite.

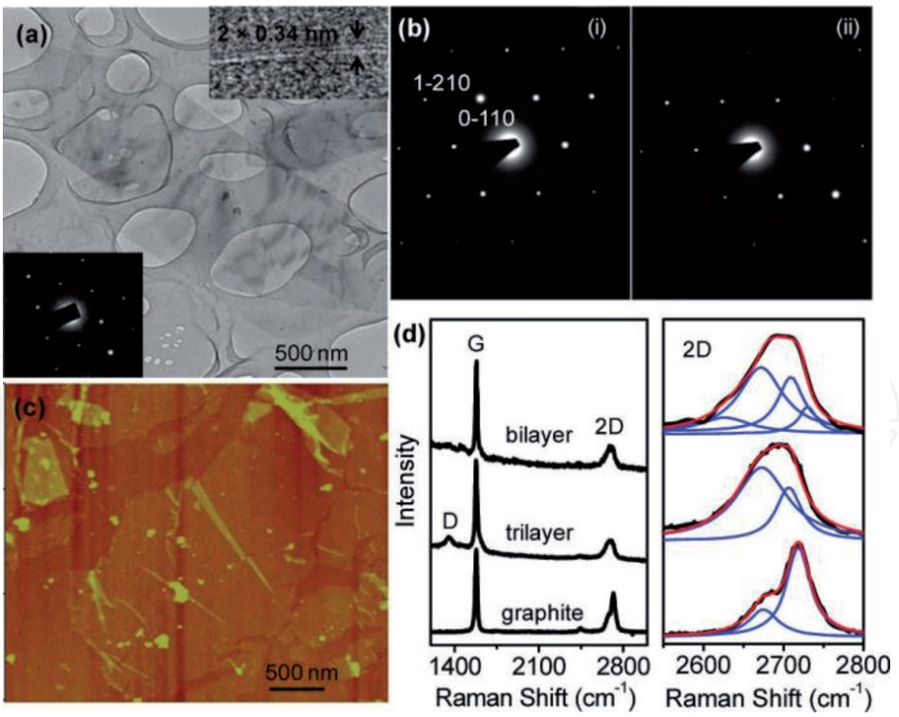

Figure 13.
(a) TEM images and electron diffraction pattern of cathodic exfoliated graphene, (b) electron diffraction patterns of (i) single and (ii) bilayer sheets, (c) AFM image of exfoliated graphene spin-coated onto a Si substrate. The thickness is ~1.5 nm, corresponding to a bilayer. (d) (left) Raman spectra (532 nm laser) on Si substrates compared with the spectrum of graphite; (right) Lorentzian peak fitting of the 2D bands of the bilayer and trilayer [44].

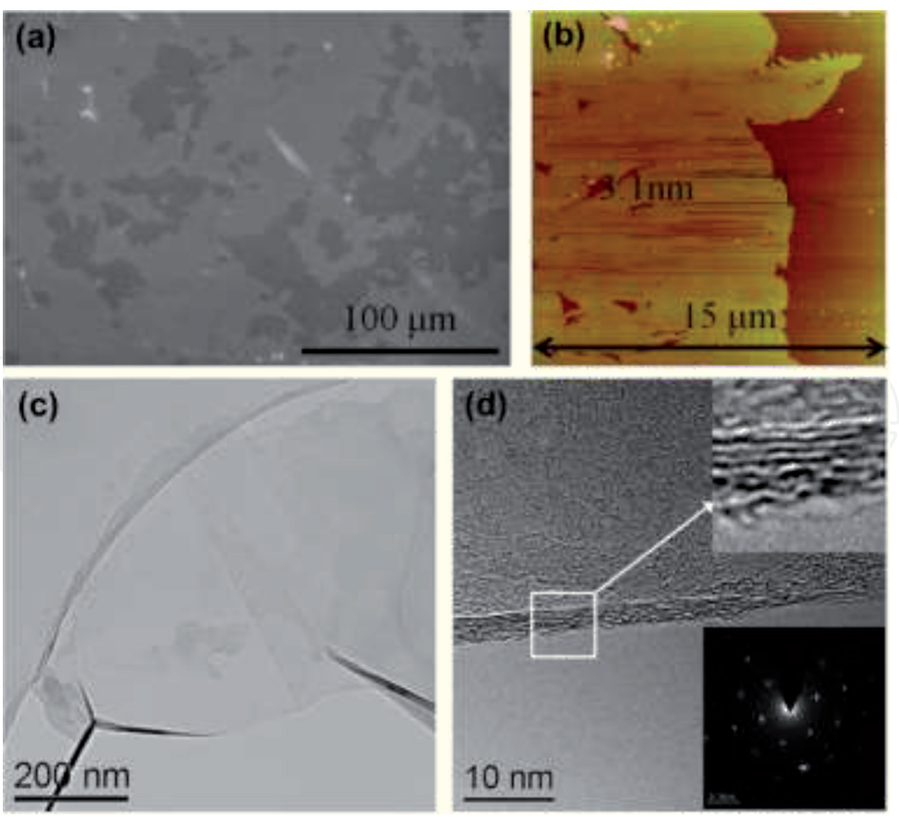

Figure 14.
(a) SEM image, (b) AFM image of graphene flakes deposited on Si substrate, (c) TEM image, and (d) HR-TEM image of a graphene flake. The inset is an electron diffraction pattern and magnified portion of the edge of the graphene flake [111].

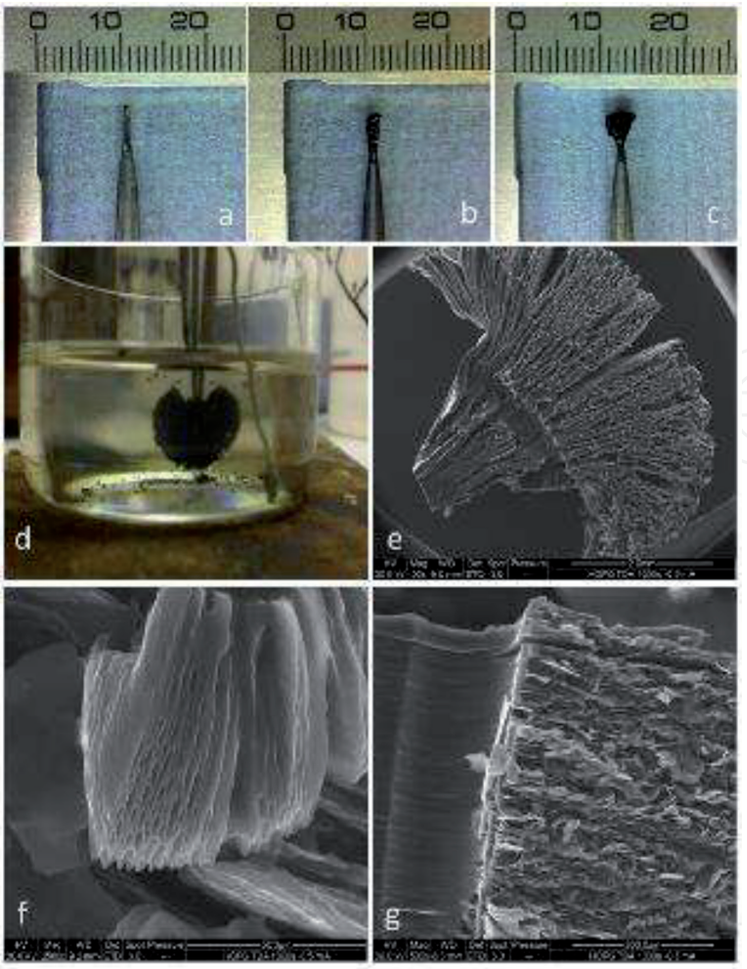

Figure 15.
(a) Photographs of as prepared HOPG, (b) HOPG expansion after 1000 s tetraethylammonium cation intercalation, (c) HOPG expansion after 1000 s tetrabutylammonium cation (TBA^+) intercalation, (a–c scale in mm) (d) HOPG expansion after 10,000 s TBA^+ intercalation, (e) SEM image of HOPG expansion after 6000 s TBA^+ intercalation, (f) SEM image showing micron-sized pores in HOPG after TBA^+ intercalation, (g) SEM image showing selective exfoliation of HOPG electrode: The point on a HOPG electrode that was held by tweezers (left-hand side) whilst the rest of the electrode (right-hand side) was submerged [57].

Zhou et al. [111] have efficiently presented, so far, the only familiar method followed to exfoliate graphitic cathodes into aqueous medium deliberately, using an electrolyte containing NaCl, DMSO, and thionin acetate salt. Sodium ions were chemically combined with (four or five) DMSO molecules, readily forming Na^+/DMSO complex-composite. Complexes so obtained were still intercalated in the form of graphene-galleries owing to graphite, clearly forming ternary graphitic-intercalation compounds ($Na^+(DMSO)_yCn^-$). Further, interlayer spacing was systematically reported to be 1.246 nm, accordingly. However, perfect exfoliation was rather not achieved through only electrochemical-treatment, therefore the sample was necessarily subjected to sonication process in order to achieve more stable graphene dispersions (**Figure 14**). In addition, however, samples were observed as heavily contaminated (with sulfur, oxygen, and nitrogen impurities).

Cooper et al. have deliberately shown tetraalkylammonium salts to be cathodic intercalation into HOPG by using relatively low potentials (ca. −2 V) [112] and maybe systematically employed to produce purely cathodic-exfoliated materials, consisting clearly (2 or 5 layers) of graphenes (see **Figure 15**) [57]. More significantly, the materials were certainly found containing (no functionality or oxidation), rather inclusion of slightly 1% in atomic form oxygen, probably induced from the atmospheric exposure of the so obtained isolated materials.

Further, Yang et al. [113] employed a pure ionic-liquid, N-butyl, methylpyrrolidinium bis (trifluoromethylsulfonyl)-imide (BMP TF_2N) towards cathodic-graphitic intercalation/exfoliation mechanism. In authors' view, $[BMP]^+$ cations chemically intercalated between the highly negatively charged (graphene layers), causing the expanded interlayer spacing. The aforesaid expansion facilitates the bigger molecules insertion, such as the $BMPTF_2N$ ion-pair, subsequently, caused by higher expansion in graphite as well. The authors have certainly claimed that formation of graphene sheets was consisted of between (two and five layers), with 2.5% atomic-oxygen yet free defected materials. However, the authors, not suggested a reasonable explanation for the gel-like-phase, probably formed from the ionic- liquid during which (the cations or anions) are expected to be consumed in all irreversible reactions [114, 115].

4. Conclusions

The process of electrochemical exfoliation has been confirmed to operate in a wide variety of layered materials; the majority of studies are conducted on large-sized bulk single-crystals, which are costly and inefficient for industrial applications. Small-sized powders or flakes are readily produced from natural materials or industrial synthesis should be considered as an alternative for efficient and successive exfoliation. Both aqueous and non-aqueous electrolytes are employed to exfoliate layered materials, but the procedure is more often used in aqueous solutions and under anodic conditions for the exfoliation of graphite owing to better performance relative to cathodic scheme, in this technique most reliable and effective way is Li-ion insertion. Around the same time, a deeper understanding of process/mechanism of intercalation and exfoliation of powered by application of current is desperately required, which may encourage the use of electrochemical means to exfoliate more effectively a large number of layered materials.

Conflict of interest

Authors have declared no 'conflict of interest'.

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