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REVIEW

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Synthesis of graphene materials by electrochemical exfoliation: Recent progress and future potential

Fei Liu[1,2] | Chaojun Wang[1] | Xiao Sui[1] | Muhammad Adil Riaz[1] | Meiying Xu[2] | Li Wei[1] | Yuan Chen[1]

[1]School of Chemical and Biomolecular Engineering, The University of Sydney, Sydney, New South Wales, Australia

[2]Guangdong Provincial Key Laboratory of Microbial Culture Collection and Application, State Key Laboratory of Applied Microbiology Southern China, Guangdong Institute of Microbiology, Guangdong Academy of Sciences, Guangzhou, China

Correspondence
Li Wei and Yuan Chen, School of Chemical and Biomolecular Engineering, The University of Sydney, Sydney, New South Wales 2006, Australia.
Email: l.wei@sydney.edu.au (L.W.) and yuan.chen@sydney.edu.au (Y.C.)

Meiying Xu, Guangdong Provincial Key Laboratory of Microbial Culture Collection and Application, State Key Laboratory of Applied Microbiology Southern China, Guangdong Institute of Microbiology, Guangdong Academy of Sciences, Guangzhou, China, 510070.
Email: xumy@gdim.cn

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Abstract

Synthesis of structurally controlled graphene materials is critical for realizing their practical applications. The electrochemical exfoliation of graphite has emerged as a simple method to produce graphene materials. This review examines research progress in the last 5 years, from 2015 to 2019. Graphene material synthesis methods generally have a trade-off between increasing production yield and achieving better material property control. The synthesis conditions for synthesizing pristine graphene, graphene oxide (GO), and graphene composites are significantly different. Thus, in this review, we first discuss synthesis methods for graphene materials with high C/O ratios from four aspects: graphite electrodes, equipment engineering, electrolytes, and additional reduction methods. Next, we survey synthesis methods for GO and examine how the pretreatment of the graphite electrodes, electrolytes, and operation parameters, such as applied voltages, electrolyte temperatures, and mechanical forces, affect the quality of GO. Further, we summarize electrochemical exfoliation methods used to dope graphene materials, introduce covalent functional groups, incorporate various nanoparticles, and assembly of graphene architectures. For all synthesis methods, we compare the properties of resulting graphene materials such as C/O ratios, lateral size, layer numbers, and quality characterized by Raman spectroscopy. Lastly, we propose our perspectives on further research. We hope this review stimulates more studies to realize the on-demand production of graphene materials with desired properties using electrochemical exfoliation methods.

KEYWORDS

electrochemical exfoliation, graphene, graphene oxide, graphite, synthesis

1 | INTRODUCTION

Graphene, ideally, is a single-atom-thick sheet of sp^2-bonded carbon atoms arrayed in a hexagonal lattice. The substantial π-electron conjugation in graphene results in fascinating electronic, thermal, magnetic, optical, mechanical, and chemical properties.[1-4] The most widely used derivative of graphene, graphene oxide (GO), is a

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chemically modified graphene material with abundant O-containing functionalities on its basal planes and edges, typically having lower C/O atomic ratios. Reduced GO (rGO) is obtained by the extensive reduction of GO using different methods, yielding a significantly lower O content compared to GO. Free-standing graphene was first isolated from graphite by micromechanical exfoliation using scotch tapes in 2004.[1] While the intrinsic properties of graphene have been studied using micromechanical exfoliated samples, practical applications require scalable and cost-effective methods to provide structurally controlled graphene materials.

In the past 15 years, many methods have been explored to produce graphene materials, which can be categorized into two groups.[5] The first group is the bottom-up synthesis methods, by which graphene sheets are grown from individual molecules, including organic synthesis in solvents,[6,7] chemical vapor deposition of gaseous carbon precursors on solid catalytic substrates,[8-11] and graphitization of silicon carbide (SiC) crystals.[12,13] The second group is the top-down exfoliation methods. As the graphene can be considered as the core structural motif of graphite, carbon nanotubes (CNTs), and many other carbon nanomaterials, it is possible to obtain graphene materials through the exfoliation of those by mechanical, chemical, thermal, or electrical routes.[14-16] For example, an energetic ultrasound vibration can be used to overcome interplanar the van der Waals forces (5.9 kJ/mol) among graphene sheets in graphite, and exfoliated graphene sheets can be stabilized in solvents with matching surface energy, such as *N*-methyl-2-pyrrolidone and *o*-dichlorobenzene.[17-20] Alternatively, graphite can be oxidized to produce GO.[21] With relatively milder mechanical forces, GO can be exfoliated from graphite oxide and stabilized in various solvents due to repelling forces among GO sheets introduced by their surface functional groups.[21-24]

Graphene synthesis often faces a critical trade-off between the yield and the property control of resulting graphene materials.[25] For example, mechanical exfoliation of graphite without chemical functionalization has poor production yield. The resulting graphene dispersions have a concentration usually below 0.5 mg/L. In contrast, the exfoliation of graphite oxide produces GO at a much higher yield, which led to the commercialization of the technique. However, GO with surface functional groups have low C/O atomic ratios, and their properties are much different from those of graphene. Although many reduction methods can be used to produce rGO, they still cannot fully match the properties of graphene.[26,27] It remains a significant challenge to synthesize graphene materials with well-controlled properties cost-efficiently and environmentally friendly.[28,29]

In recent years, electrochemical exfoliation of graphite has emerged as a simple method to produce graphene materials.[30-33] As illustrated in Figure 1A, graphite in a variety of geometries, such as graphite powders, foils, rods, flakes, or plates, can be used as working electrodes in liquid electrolytes.[34] Depending on the power supply applied on graphite electrodes, there are cathodic (applying a negative bias) and anodic (using a positive bias) exfoliation methods. As illustrated in Figure 1B, positively charged ions in the electrolyte (eg, Li^+) would be attracted to graphite electrodes in cathodic exfoliation. Negatively charged ions (eg, SO_4^{2-}) may be attracted to electrodes in anodic exfoliation. Ions, electrolyte molecules, or cointercalating species in electrolytes are first intercalated among the graphene layers of graphite. It has been proposed that electrochemical reactions provide driving force to break the van der Waals forces, leading to the structural expansion of graphite.[35] By controlling process parameters, such as applied electrical potentials, currents, processing time, as well as the composition of electrolytes, the graphene materials of different defect densities, O contents, graphene layer numbers, and lateral sizes have been obtained. Moreover, chemical reactions with functionalizing agents can concurrently take place during electrochemical exfoliation to achieve in situ chemical doping (functionalization) of graphene materials to produce various graphene-based composite materials.

Previous review articles on electrochemical exfoliation of graphite examined the methods for synthesizing graphene and GO together and focused on their operation parameters, such as electrolytes and applied potential biases.[31,34-36] In our opinion, one of the most important criteria in evaluating graphene material synthesis methods is their capability in precisely controlling the material properties. Although their reactions and synthesis parameters are similar, the detailed requirements for synthesizing graphene and GO are significantly different. Thus, in this review, we discuss recently developed methods for graphene and GO synthesis separately. The methods used to produce graphene with high C/O ratios are discussed first, followed by the studies focused on synthesizing GO with low C/O ratios. We compare the properties of resulting graphene materials such as C/O ratios, heteroatom dopants, covalent functionalization, and hybrid/composites. Subsequently, we summarize studies on the synthesis of heteroatom doped or functionalized graphene and graphene composites using electrochemical exfoliation. Lastly, we propose our perspectives on the further development of this promising route toward the on-demand production of graphene materials with desired properties in a practical manner.

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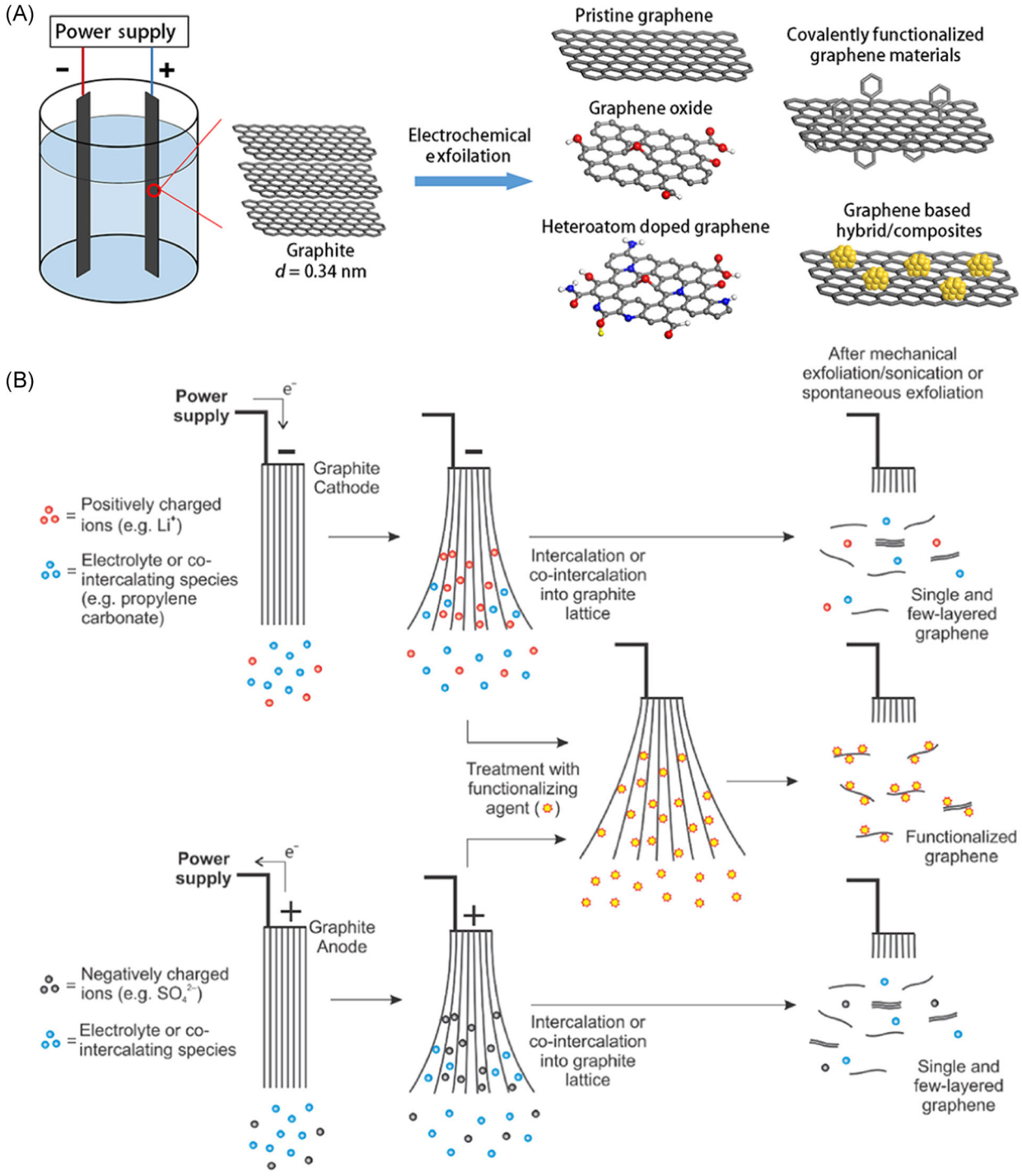

FIGURE 1 A, Schematic illustration of electrochemical exfoliation of graphite to produce various graphene materials. B, Schematic overview of cathodic and anodic exfoliation of graphite. Reprinted with permission from Yu et al,[35] Copyright 2015 Elsevier

2 | GRAPHENE SYNTHESIS BY ELECTROCHEMICAL EXFOLIATION

A key target of graphene synthesis is to produce almost pristine graphene with low O content, fewer layers, and large lateral size. However, graphite exfoliation in liquid electrolytes in ambient conditions commonly introduces O in the carbon lattice of graphene and break exfoliated graphene into small pieces. Electrochemical exfoliation methods have demonstrated some controllability in the structural properties of graphene materials.[23,37,38] In this section, we discuss the new process from four aspects: graphite electrodes, equipment engineering, electrolytes, and additional reduction methods. The operating parameters and graphene properties of several recently

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TABLE 1 A summary of recent representative studies on the synthesis of graphene materials by electrochemical exfoliation of graphite

Electrolytes	Graphite electrodes	Power supplies	Additional conditions	Properties of graphene materials				References
				C/O ratios	Size (μm)	No. of layers	I_D/I_G	
0.1M K_2SO_4	Graphite foil	Anodic, +10 V, DC	Graphite powder, HOPG	17.2	0.2-0.6	1-2 nm	0.38	[39]
0.2M $(NH_4)_2SO_4$	Graphite rod	Anodic, +10 V, DC	+2 V, DC; sonication	11.7	0.5-1	2	1.76	[40]
10M H_2SO_4	Expanded graphite	Anodic, +1 and +2 V, DC		7.5	10-30	2-4	0.3	[41]
0.1M $(NH_4)_2SO_4$	Graphite flake	Anodic, +10 V, DC	Packed in dialysis tubing	4.98	>30	2-7 nm	0.9/1.2	[42]
0.1M $(NH_4)_2SO_4$	Graphite + clay	Anodic, +10 V, DC		NA	NA	3-4	1.2-1.5	[43]
0.5M H_2SO_4	Graphite foil	Anodic, +10 V, DC	Pretreatment in 1M NaOH	11.0	2.2	2-4	0.29	[44]
0.1M H_2SO_4	HOPG	50 and 580 mA	Constant current chronopotentiometric steps	7.7	1.5	2	0.14	[45]
0.1M TBA·HSO_4, NaOH	Graphite sheet	Both, 10 V, 0.1 Hz AC		21.2	5	1-3	0.15	[46]
0.1M $(NH_4)_2SO_4$, CH_4N_2S	Graphite foil	Both, 10 V, 0.1 Hz AC	Temperature 5°C-20°C	18.1-37.1	NA	NA	0.057-0.138	[47]
0.1M sodium saccharin	Graphite rod	2, 4, 6, 8, 10 V chronoamperometry	Anodic interalcation + cathodic reduction	NA	NA	3.36-4.49 nm	1.1	[48]
0.1M $(NH_4)_2SO_4$	Graphite foil	anodic, +15 V, DC		8	1	1-2	0.4	[49]
0.1M C_6H_5COOH (C_6H_5COONa), 0.1M Na_2SO_4	Graphite rod	+3 and −1.5 V (20 s)	Pulse electrolysis	25	2-5	13	0.28	[50]
0.25M H_2SO_4, KOH	Graphite foil	Anodic, +10 V, DC	Heated to 80°C	NA	NA	3	0.33	[51]
0.5M $(NH_4)_2SO_4$	Graphite foil	Anodic, +30 V, DC	Lifting electrolyte	8	0.3-5.0	<3	0.8	[52]
0.1M H_2SO_4	HOPG	Anodic, +1 to 10 V, DC	Shear field (up to 74 400 s^{-1})	NA	10	1-3	0.21-0.32	[53]
0.01M-5M $(NH_4)_2SO_4$	Graphite flake	Anodic, +10 V, DC	Compare different salts	17.2	5	1-3	0.42	[54]
0.1M $(NH_4)_2SO_4$	Graphite rod	Anodic, +10 V, DC	Inkjet printing ink	NA	0.5-0.65	2 nm	NA	[55]
0.05M NaCl (0.1M NaBr, 0.1M NaI)	Graphite foil	Anodic, +10 V, DC		16.7	0.6	2-3 nm	0.8	[56]
0.1M Na_2SO_4, 0.1M NaCl	Graphite foil	Anodic, +10 V, DC		33.3-50	1	<5	0.21	[57]
0.5M Na_2SO_4	Graphite foil	Anodic, +20 V, DC	0.05M $CoSO_4$	36	NA	1 and few	0.05	[58]
Sulfonate-/sulfate-hydrocarbons (eg, 0.2M SNDS)	Graphite foil	Anodic, +10 V, DC		50		2.5 nm	0.2	[59]
1M $Na_2S_2O_3$, 0.5M $NaClO_4$, 0.5M NaOH	Graphite sheet	Anodic, +10 V, DC		27.7	4	4-6	0.35	[60]
13.5 wt.% H_2SO_4, 30 wt.% KOH	Graphite plate	Both, 15 V DC	0.11 A/cm^2, sonication	NA	NA	6	0.061	[61]
0.2M H_2SO_4, 30 wt.% KOH	Graphene flakes	Both, 10-15 V, 1 A, 0.2 Hz AC		NA	3.7	2.5 nm	NA	[62]

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TABLE 1 (Continued)

Electrolytes	Graphite electrodes	Power supplies	Additional conditions	Properties of graphene materials				References
				C/O ratios	Size (μm)	No. of layers	I_D/I_G	
0.05M $(NH_4)_2SO_4$, 50 mg TEMPO in 50 mL H_2O	Graphite foil	Anodic, +10 V, DC		25.3	5-10	1-3	0.1	[63]
0.5 g HCPCP in 100 mL H_2O, NaOH	Graphite flake	Anodic, +10 V, DC		10.4	NA	NA	1.42	[64]
Gly•HSO_4/H_2O (15:85)	Graphite rod	Anodic, +1 and 3 V, DC		8.1	NA	2-5	0.70	[65]
37.4 wt.% acetamide, 28 wt.% urea, 34.6 wt.% NH_4NO_3	Graphite foil	CV, −0.6-1.5 V		7.3	0.2-0.4	1-5	0.60	[66]
6.5 g H_2SO_4/100 mL H_2O, melamine (10-200 g/100 mL)	Graphite powder	20 V, AC		26.17	18	<3	0.20-0.45	[67]
0.1M ionic liquids in acetonitrile	Graphite rod	Both, 10-20 V, DC	H-cell	NA	0.5-0.8	5	NA	[68]
Deep eutectic solvents, BMPyrrBTA, acetonitrile	Graphite rod	Anodic, +7 V, DC	$ZnNO_3 6H_2O$/urea (1:2)	NA	NA	4-5	NA	[69]
8M $HClO_4$	Graphite flake	LSV, 1.4 V	Thermal reduction at 500°C	19.6	0.15	6-7	0.59	[70]
0.1M $(NH_4)_2SO_4$	Graphite rod, HOPG	Anodic, +12 V, DC	Thermal reduction up to 800°C	13.9/13.5	NA	NA	1	[71]
1.0M H_2SO_4	Graphite foil	Anodic, +3 V, DC	Spark plasma treatment	25.3	NA	1-2	0.16	[72]
Urea, choline chloride, LiCl	Graphite rod	−2.5 V, chronoamperometry		NA	NA	1.1 nm	NA	[73]

Abbreviations: AC, alternating current; BMPyrrBTA, 1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) imide; CV, cyclic voltammetry; DC, direct current; HCPCP, hex(4-carboxylphenoxy) cyclotriphosphazene; HOPG, highly oriented pyrolytic graphite; LSV, linear sweep voltammetry; NA, not available; SNDS, sodium naphthalene 1,5-disulfonate; TBA·HSO_4, tetra-*n*-butylammonium bisulfate; TEMPO, (2,2,6,6-tetramethylpiperidin-1-yl) oxyl.

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reported representative graphene synthesis methods are summarized in Table 1.

2.1 | Graphite electrodes for graphene synthesis

Commonly used graphite electrodes in electrochemical exfoliation are either natural graphite in forms of foils, rods or sheets or highly oriented pyrolytic graphite (HOPG). The electrochemical exfoliation of graphite relies on efficient ion intercalations among graphene layers to expand their interlayer spacing. Ion intercalations are expected to be influenced by graphite electrodes' microstructures, such as graphite particulate sizes, defects, layer arrangements, and thickness, composition, and suitable pretreatment. Several recent studies have explored how these parameters affect graphene synthesis.

Munuera et al showed that structural imperfections in graphite foils, such as folds, voids, and wrinkles, would facilitate the exfoliation of graphite and reduce damages caused by oxidative reactions during electrochemical exfoliation. Figure 2 shows that defective graphite foils produced graphene materials with one to two graphene layers, which have better quality than those produced from HOPG electrodes with much fewer structural imperfections.[39] Fuertes et al reported that thick graphite rods or sheets are usually exfoliated at considerably lower rates than thin graphite foils or flakes. The slower exfoliation rate fosters graphite oxidation, resulting in more hydrophilic graphene materials. When a graphite rod was used as an anode, well-dispersed bilayer graphene sheets were obtained with a C/O ratio of 11.7, and the average lateral size of bilayer graphene sheets is about 0.5 to 1 μm.[40] Similarly when expanded graphite was exfoliated, graphene materials show a relatively lower C/O ratio of 7.5.[41]

As illustrated in Figure 3, Green et al showed that graphite rod electrodes would disintegrate during electrochemical exfoliation. Graphite particles detached from electrodes usually cannot be further exfoliated, resulting in poor exfoliation efficiency. They contained and compressed small graphite flakes within a permeable and expandable dialysis tube. Graphite flakes can be continuously intercalated, expanded, and exfoliated to produce graphene materials, which produced graphene materials with extraordinarily large lateral size (>30 μm) and a C/O ratio of 4.98.[42] Pencil cores are physical mixtures of graphite and clays. Chen et al[43] showed that graphite/clay mixtures in pencil cores could serve as efficient graphite electrodes for graphene synthesis by electrochemical exfoliation. The exfoliated graphene materials can migrate to the top of the electrolyte while the clays precipitate at the bottom along with unexfoliated graphite. Thus, it is easy to separate graphene products from unexfoliated materials.

Selective pretreatment or adopting proper interaction steps for graphite electrodes may be beneficial to yield desirable graphene materials. For example, Fang et al found that pretreatment of graphite electrodes using alkaline solutions can significantly reduce graphite oxidation during electrochemical exfoliation in acidic electrolytes. They first immersed graphite foils in NaOH solution and then exfoliated them in H_2SO_4 electrolyte, which yielded few-layer graphene materials with a high C/O ratio of 11.02.[44] It was proposed that the pretreatment in NaOH can increase interlayer spacing in graphite. Neutralization

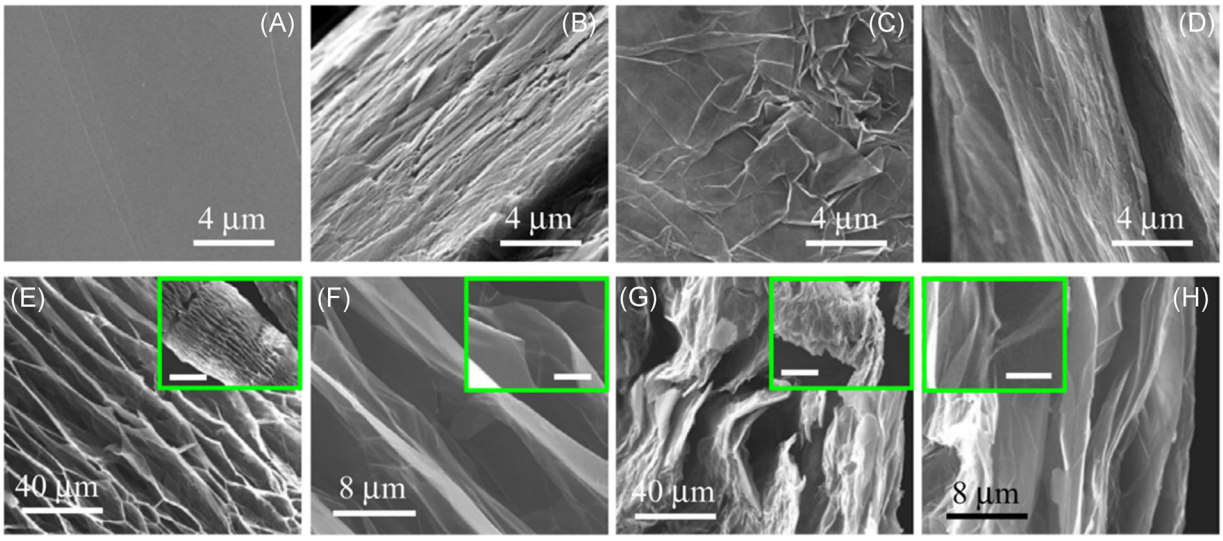

FIGURE 2 Representative SEM images of basal (A, C) and edge (B, D) surfaces of HOPG (A, B) and graphite foils (C, D) and of the edge surfaces of HOPG (E, F) and graphite foils (G, H) after electrochemical exfoliation treatment for 15 minutes. Scale bars of the inset images: 200 μm (E, G) and 1 μm (F, H). Reprinted with permission from Munuera et al,[39] Copyright 2015 Elsevier. HOPG, highly oriented pyrolytic graphite; SEM, scanning electron microscope

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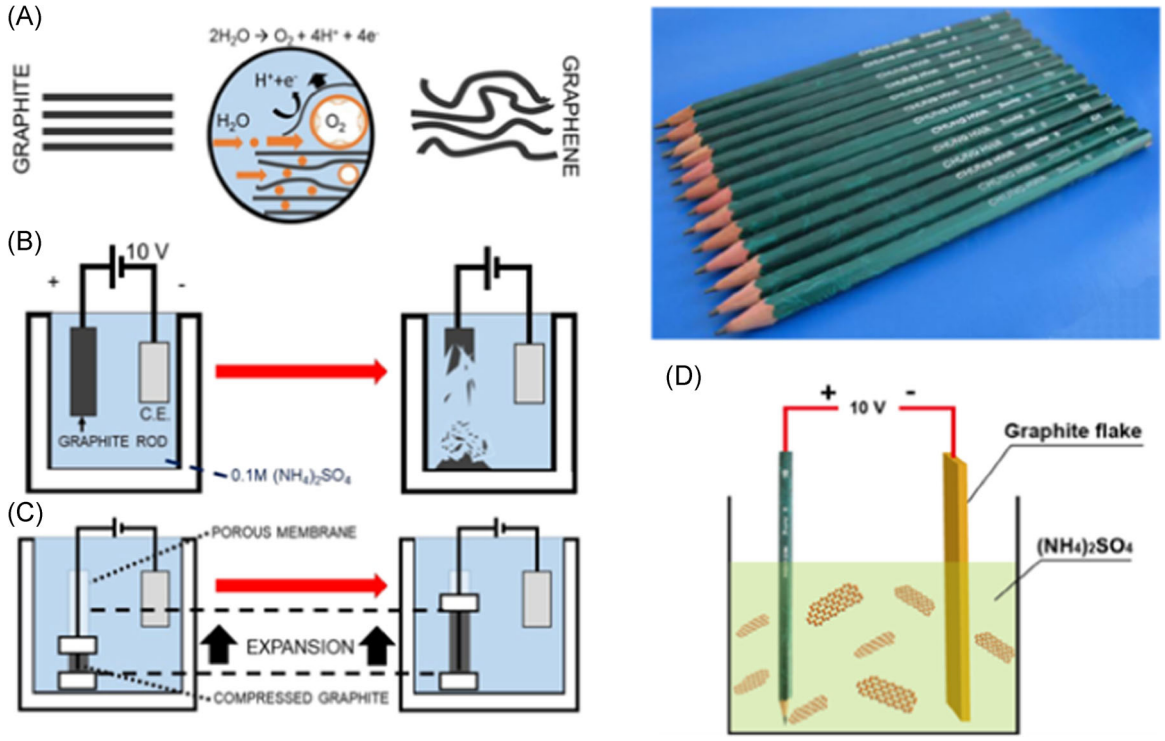

FIGURE 3 A, Schematic illustration of the electrochemical exfoliation of graphite. B, Disintegration of graphite rods during electrochemical exfoliation. C, Electrochemical exfoliation of graphite flakes in a permeable, expandable container. Reprinted with permission from Achee et al,[42] Copyright 2018 Nature. D, The electrochemical exfoliation of graphite in pencil cores. Reprinted with permission from Chen et al,[43] Copyright 2017 Elsevier

reaction between NaOH and H_2SO_4 would also produce H_2O among graphene layers to further expand interlayer spacing. Shukla et al used a HOPG electrode as the working electrode, a Pt wire as a counter electrode, an Ag/AgCl reference electrode, and H_2SO_4 electrolyte. They first applied a constant current of 50 mA to intercalate HSO_4^- ions into HOPG. Next, the intercalated electrode was exfoliated under the current of 580 mA to produce graphite flakes. They claimed that these graphite flakes contained alternating weak and strong attraction between two adjacent layers. Thus, graphene materials enriched with bilayer graphene can be obtained by sonication.[45]

In summary, to synthesize graphene, graphite electrodes should be exfoliated quickly, so that damages caused by oxidative reactions during electrochemical exfoliation can be minimized. In principle, defective, thin, and small graphite flakes could be more efficient to yield graphene materials with higher C/O ratios. Further, the pretreatment of graphite electrodes should also avoid using strong oxidative conditions.

2.2 | Equipment engineering for graphene synthesis

A variety of electrochemical equipment has been used to synthesize graphene by exfoliating graphite. They can be roughly categorized into anodic or cathodic exfoliation methods based on whether graphite electrodes are used as an anode or a cathode. Typically, anodic exfoliation methods show a higher efficiency in intercalation and expanding interlayer spacings in graphite electrodes because the reduction of water at anodes generates hydroxyl ions (OH^-), which act as a strong nucleophile and create damages in sp^2 carbon structures of graphene. Cathodic exfoliation methods induce much fewer damages in graphene; however, the exfoliation efficiency is much lower. Previous reviews have compared the differences between these two types of exfoliation methods in detail.[31,36] Thus, in this section, we focus on the electrochemical exfoliation equipment, including alternating current (AC) power supplies, voltages applied, exfoliation time, heating electrolytes, and several innovative equipment designs.

2.2.1 | Equipment operation parameters

Two types of power supplies have been used in the electrochemical apparatus, including direct current (DC) or AC ones. Feng et al used AC power supplies combined with suitable conductive media (ie, tetra-*n*-butylammonium bisulfate [TBA·HSO_4]) to achieve both high production efficiency and high quality in graphene

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synthesis from both electrodes.[46] As illustrated in Figure 4, there are different intercalation routes for graphite anodes and cathodes under AC power supplies. O-containing radicals (such as HO• and O•) are generated at graphite/water interfaces on anodes, which attack boundaries or intrinsic defects in graphite. The intercalation of sulfate anions increases the d-spacing to 0.46 nm. Intercalated sulfate anions are reduced to gas bubbles when the anodic potential switches to negative. Large TBA^+ cations are intercalated into gaps created by the gas bubbles. In contrast, the flattened TBA^+ cations (0.47 nm) are accommodated between graphene layers in cathodes. Sulfate ions are intercalated when the working bias shifts to positive. Once both anode and cathode are expanded to some extent, the complex electrochemical reactions taking place between graphene layers generate massive bubbles (O_2, H_2, SO_2, and CO_2), resulting in efficient graphene production. The resulting graphene materials are mainly composed of one to three graphene layers (75%) with a high C/O ratio of 21.2.[46] Further, using similar AC power supplies, Wang et al added thiourea (CH_4N_2S) into the $(NH_4)_2SO_4$ electrolyte and to deposit S particles on resulting graphene materials. It was proposed that S would react with radicals (eg, HO•) to form S particles, which helps to control the exfoliation of graphite.[47]

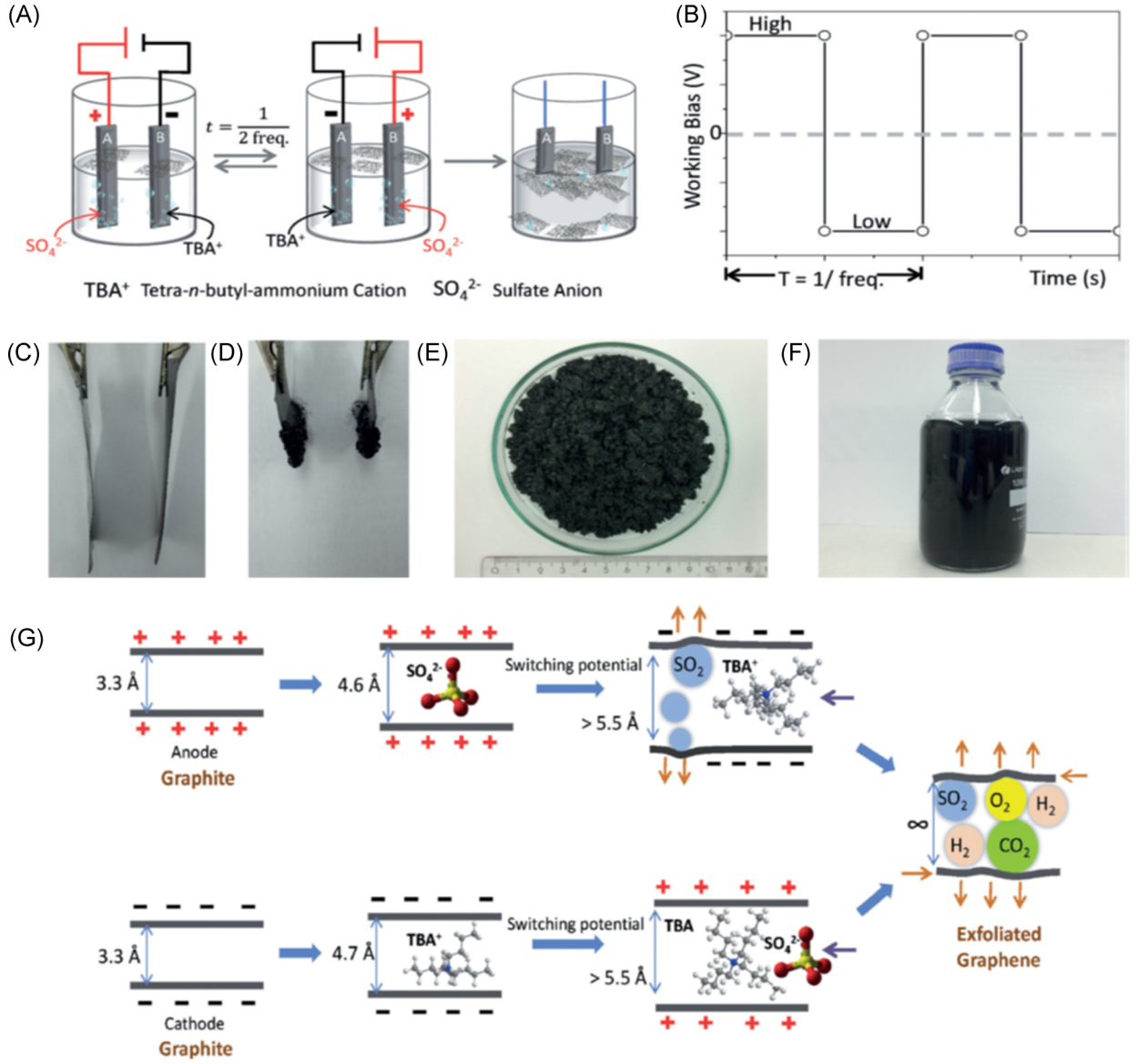

FIGURE 4 A, Schematic illustration of graphite exfoliation under AC power supplies in an aqueous solution of $TBA{\cdot}HSO_4$. B, AC working bias applied at the anode. C, D, Optical images of graphite foil electrodes before and after exfoliation. E, Graphene materials produced in 15 minutes. F, Graphene materials dispersed in DMF (0.10 mg/mL). G, A proposed mechanism for graphite exfoliation in both electrodes under AC working bias. Reprinted with permission from Yang et al,[46] Copyright 2017, Wiley-VCH. AC, alternating current; DMF, dimethylformamide; $TBA{\cdot}HSO_4$, tetra-*n*-butylammonium bisulfate

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Voltage potential and exfoliation time are expected to influence graphene synthesis. Srivastava et al compared five different voltage potentials from 2 to 10 V using a chronoamperometry technique. Graphite rods were first used as anodes to be intercalated with saccharin anion. Then, the intercalated graphite electrodes were used cathodes to be reduced. Their results showed that applying higher voltage potentials on graphite electrodes would increase the yield of graphene; however, the quality of graphene becomes lower with higher defect density and O contents due to intensified oxidation under high voltage potentials.[48] Eredia et al[49] showed that the exfoliation time in aqueous electrolyte affects C/O ratios in graphene materials. Specifically, an exfoliation time of 1 or 60 minutes results in graphene materials with C/O ratios of 8 or 4, respectively. Kurys et al applied pulse power supplied to reduce the oxidation of graphene during prolonged exfoliation in the electrolysis mode. Graphene materials with a high C/O ratio of 25 were obtained. However, they are mainly made up by multilayer graphene (10-20 layers).[50] Tripathi et al[51] demonstrated heating assisted electrochemical exfoliation method. The production yield increased 4.5 times from 17% to 77% when the electrolyte temperature was increased from room temperature to 80°C. It was proposed that the heated electrolyte may enhance the vibration of intercalated ions and increase interlayer spacings between graphene layers.

2.2.2 | New equipment designs

Several innovative device designs have also been explored to increase graphene synthesis yield and control structures of graphene materials. Xu et al proposed an end-face electrochemical exfoliation device, in which the end of graphite foils was placed in contact with the electrolyte top surface continuously during the exfoliation. As shown in Figure 5A, the container of electrolyte rose steadily to maintain contact with a graphite electrode when graphite foils disintegrated into graphene materials. It was proposed that the confined area at air-electrolyte interface provided uniform current density, resulting in graphene materials with few-layers (<3 layers) and an average lateral size of 0.3 to 5.0 μm.[52] Other than compressing graphite flakes inside a permeable container, Green et al also designed a batch reactor (Figure 5B) to increase the surface-to-volume ratio of the electrode to reduce the mass transfer limitation of electrolyte ions. A platinized Ti mesh was inserted into the graphite electrode. The electrolyte was forced to go through the graphite electrode plate. For achieving continuous graphene production, they also proposed a screw reactor as shown in Figure 5C, and the electrolyte is forced to go through a porous pipe or ridged mesh under pressure, while graphite flakes would be in contact with an in-line screw conveyer, which also works as the working electrode.[42] Alternatively, Majumder et al demonstrated a shear-assisted electrochemical exfoliation process. As shown in Figure 5D, sulfate ions were intercalated into the graphite working electrode, while shear induced by a flowing electrolyte assisted the exfoliation of graphene. Low defect, large and thin graphene flakes can be produced using modest shear and low bias potentials.[53]

In summary, electrochemical equipment should be designed to achieve a balance between the production yield and quality of graphene materials. Cathodic exfoliation, low voltage, or pulse power supplies can help to reduce damages in graphene; however, they are often accompanied by lower production yield. External means, such as high-temperature electrolytes and strong mechanical forces, which can facilitate the exfoliation of graphite without introducing additional oxidative damages to graphene, are also beneficial for graphene synthesis.

2.3 | Electrolytes for graphene synthesis

Aqueous acids, such as H_2SO_4 is the most widely used electrolyte for the electrochemical exfoliation of graphite to synthesize graphene because SO_4^{2-} (0.46 nm) are relatively easy intercalated into graphite due to the comparable ionic size with graphite d-spacing (0.34 nm). Some studies have proposed that the decomposition of SO_4^{2-} during the exfoliation generates various gaseous products, such as SO_2, O_2, and H_2, which drive the expansion of graphite interlayer spacings.[54,74] Other protic acids, such as phosphoric, oxalic, and perchloric acids, show comparable graphite exfoliation results.[41] However, the fast intercalation and decomposition of these anions often result in incomplete graphite intercalation and disintegration of graphite electrodes. Subsequently, the synthesized graphene materials have small lateral sizes and large layer numbers. Different electrolytes have been studied to control the intercalation of graphite and the decomposition of anions. We discuss the recent progress specifically on using salts and alkali in electrolytes, adding organic compounds in electrolytes, and creating in situ reduction conditions in the following three subsections.

2.3.1 | Salts and alkali in electrolytes

Different types of inorganic or organic salts have been used in electrolytes for graphene synthesis, including ionic liquids (ILs), sulfate salts, halides, transition metal

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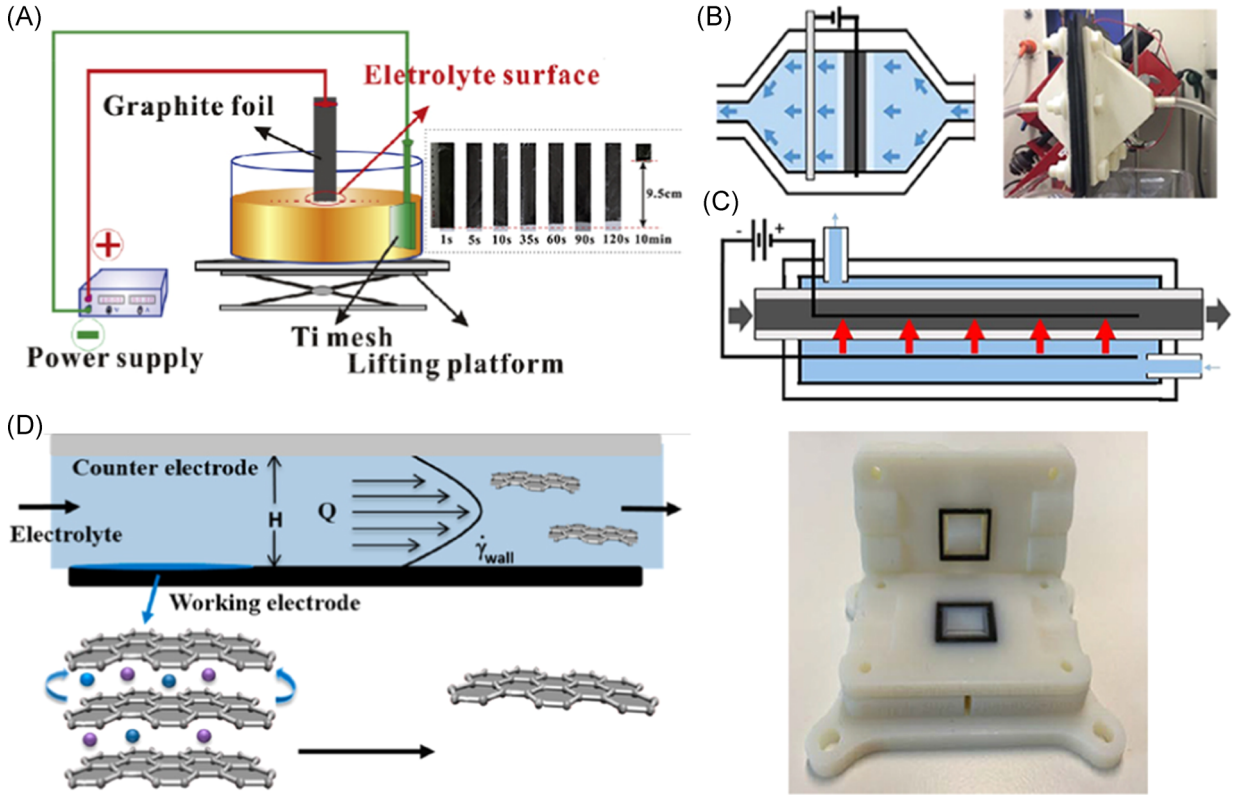

FIGURE 5 A, Schematic illustration of the end-face electrochemical exfoliation device, the inset photo shows the length change of the graphite foil electrode. Reprinted with permission from Zhou et al,[52] Copyright 2019 Elsevier. B, Schematic illustration (left) and photo (right) of a batch reactor for forced electrolyte flow through a tileable 2D graphite electrode with platinized Ti mesh. C, Schematic design of permeable plug-flow reactor with forced electrolyte flow for continuous production of graphene by electrochemical exfoliation. Reprinted with permission from Achee et al,[42] Copyright 2018 Nature. D, Schematic illustration (left) and photo (right) of microreactor used for electrochemical exfoliation with a shear force on the reactor walls. Reprinted with permission from Shinde et al,[53] Copyright 2016 ACS

salts, and salts containing amphiphilic anions. Other than ILs, various ions strongly affect the properties of graphene materials by reacting with oxidative radicals generated during graphite exfoliation. Besides, some amphiphilic anions provide additional functions in improving the dispersion of graphene flakes.

ILs are salts in the liquid state. Several early studies have used ILs as electrolytes to exfoliate graphite.[75-77] However, the production yield of graphene is usually low, and the lateral size of graphene is also small (<5 μm). Other carbon materials, such as carbon nanoribbons and nanoparticles, were also produced when using ILs as electrolytes. Water content in ILs was found to play a critical role in the properties of resulting carbon nanomaterials. Concentrated ILs may functionalize carbon nanomaterials, which disrupt their electronic properties. ILs with high water content (>10 wt.%) would produce water-soluble and oxidized carbon nanomaterials.[76]

Parvez et al[54] compared aqueous solutions containing different sulfate salts, including $(NH_4)_2SO_4$, Na_2SO_4, and K_2SO_4, under neutral pH conditions. $(NH_4)_2SO_4$ was found to be the best salt for electrolyte, which yielded graphene materials mostly composed of one to three monolayers (~85%) with sizeable lateral size (>5 μm) and a high C/O ratio of 17.2. The effect of electrolyte concentration was further studied. When the concentration of $(NH_4)_2SO_4$ was lower than 0.01M, the yield of graphene materials was less than 5 wt.%. In 1.0M $(NH_4)_2SO_4$, 75 wt.% graphene yield was achieved. A further increase in the concentration failed to rise the graphene production yield. It was proposed that the high concentration of $(NH_4)_2SO_4$ would suppress the formation of OH^- ions due to the low water content, which lowers the graphite edge oxidation and expansion.[54] A 0.1M $(NH_4)_2SO_4$ aqueous electrolyte was also used to produce graphene nanoplatelets.[55] The graphene materials can be well dispersed in dimethylformamide for inkjet printing. Munuera et al[56] showed that aqueous solutions containing sodium halides (ie, NaCl, NaBr, or NaI) can be used as electrolytes for anodic exfoliation of graphite, which yielded single-/few-layer graphene materials with a C/O ratio up to 16.7. Hydrated halide anions can be intercalated in graphite foil electrodes. The halide anions

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also acted as sacrificial agents to react with HO• radicals, which limited the attack of HO• radicals on graphite lattice, leading to graphene nanosheets with low O content. The concentration of sodium halides is also critical. Graphite electrodes were poorly intercalated at low salt concentration, while electrodes would be disintegrated due to the very dynamic and fast intercalation process at high salt concentrations. The optimal concentrations are 0.05M, 0.1M, and 0.1M for NaCl, NaBr, and NaI, respectively.[56] Some transition metal ions have been identified to act as an effective antioxidant during graphite exfoliation, which can prevent surface oxidation of graphene. In a recent study, Munuera et al[57] added NaCl or KCl as coelectrolyte to Na_2SO_4, which showed much better efficiency than NaBr, NaI, Na_2SO_3, sodium citrate, ascorbic acid, $NaBH_4$ and ethanol in preventing the oxidation of graphene, yielding graphene materials with one of highest C/O ratios (33.3-50) ever reported. Dryfe et al added 0.05M $CoSO_4$ to 0.5M Na_2SO_4 as electrolytes. While sulfate anions were intercalated tin to graphite, Co^{2+} was converted to Co^{4+} under the oxidative potential at anodes. Co^{4+} may oxidize water to O_2 without the formation of OH• intermediate, thus reducing graphite surface oxidation. Adding of $CoSO_4$ lowered the C/O ratio by a factor of 5 to reach 36.[58]

Villar-Rodil et al explored the concept of multifunctional electrolytes, in which amphiphilic anions, such as polyaromatic hydrocarbons appended with sulfonate groups, can play several different roles together. Intercalating ions would trigger the exfoliation of graphite. A dispersant helped to stabilize aqueous colloidal suspensions of graphene flakes. As illustrated in Figure 6, a sacrificial component in the electrolyte prevented graphene oxidation during exfoliation. A linker in the electrolyte promoted nanoparticle anchoring on the graphene flakes to produce functional hybrids. They studied 13 sulfonate- and sulfate-containing hydrocarbons at different concentrations. When 0.2M sodium naphthalene 1,5-disulfonate was used as an electrolyte, graphene materials with an ultrahigh C/O ratio of 50 were obtained.[59]

Since acidic electrolytes would create significant defects in graphene materials, adding suitable bases in electrolytes has been used to change the pH of electrolytes and facilitate the electrochemical reduction of functional groups on the graphene surface. For example, Parveen et al[60] used an aqueous mixture of NaOH, $Na_2S_2O_3$, and $NaClO_4$ as electrolytes for graphite exfoliation. It was proposed that $NaClO_4$ expanded the graphite lattice, NaOH reduced functional groups and $S_2O_3^{2-}$ accelerated the exfoliation of graphite. The resulting graphene materials showed a high C/O ratio of 27.7. Liu et al studied the ratios between KOH and H_2SO_4 and showed that the mixture of 30 wt.% KOH and 13.5 wt.% H_2SO_4 had the best exfoliation efficiency. The resulting graphene materials had a low I_D/I_G ratio of 0.061.[61] Kong et al also studied the ratios between KOH and H_2SO_4. The optimum result was achieved by using 30 wt.% KOH. The resulting graphene materials showed a high lateral size (3.7 μm) to thickness ratio (2.5 nm).[62]

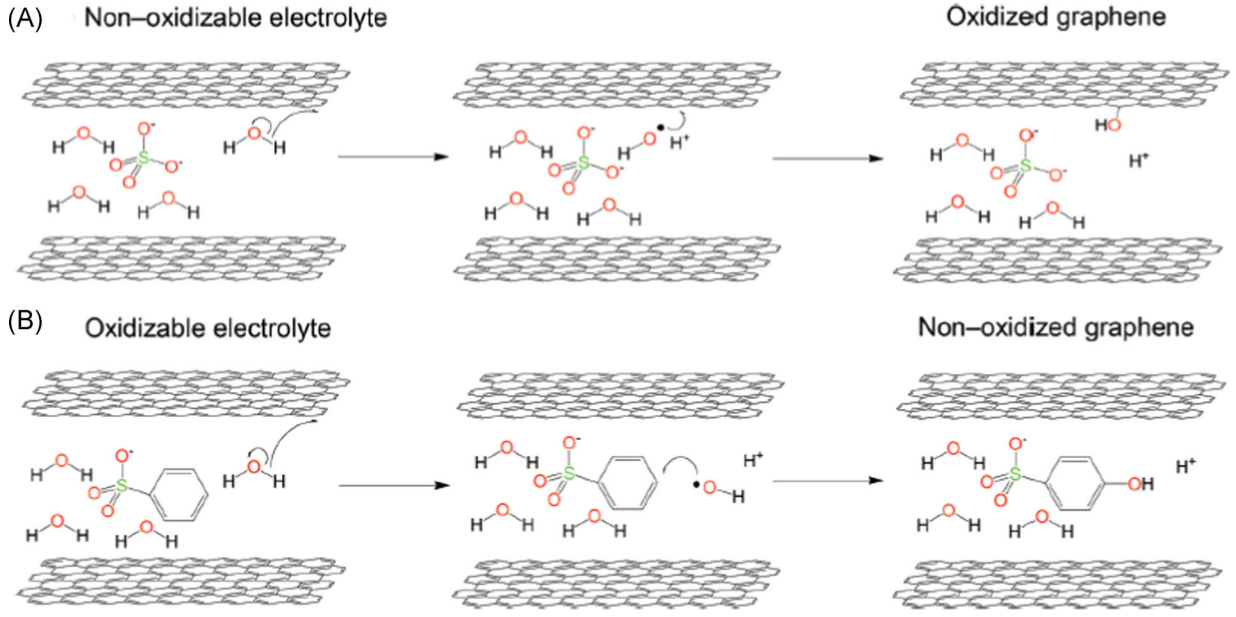

FIGURE 6 Schematic illustration of the roles of different electrolytes. A, Water in nonoxidizable electrolytes, such as Na_2SO_4, would create reactive OH• and O• radicals, which attach graphene layers. B, Oxidizable electrolytes, such as SBS, would act as a sacrificial agent to hinder the oxidation of graphene. Reprinted with permission from Munuera et al,[59] Copyright 2016 RSC

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2.3.2 | Organic compounds in electrolytes

Other than adding salts and alkali in electrolytes, some organic compounds have been explored to limit the oxidation of graphene to improve the quality of graphene materials. Yang et al[63] introduced organic reducing agents in aqueous $(NH_4)_2SO_4$ electrolytes. They compared ascorbic acid, gallic acid, hydrazine, sodium borohydride, hydrogen iodide, and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO). As illustrated in Figure 7A, the HO• radicals can react with TEMPO to form metastable intermediates (TEMPO-OH), which then were converted to oxoammonium cations. The oxoammonium cations can be electrochemically reduced at the cathode to form TEMPO radicals again. The resulting graphene materials have a high C/O ratio of 25.3, low I_D/I_G ratio of 0.1, and large lateral size of 5-10 μm.[63] Similarly, Hu et al used a flame retardant (hex(4-carboxylphenoxy) cyclotriphosphazene [HCPCP]) dissolved in NaOH aqueous solution as the electrolyte. HCPCP can act as an antioxidant during graphite exfoliation, resulting in graphene materials with a high C/O ratio of 10.4.[64]

On the contrary, organic compounds can also be used to enhance exfoliation efficiency. As shown in Figure 7B, Yoshimura et al used glycine (Gly)·HSO_4 ionic complex to facilitate the intercalation of HSO^{4-} and SO_4^{2-} ions into graphite electrodes. The intercalated ions underwent

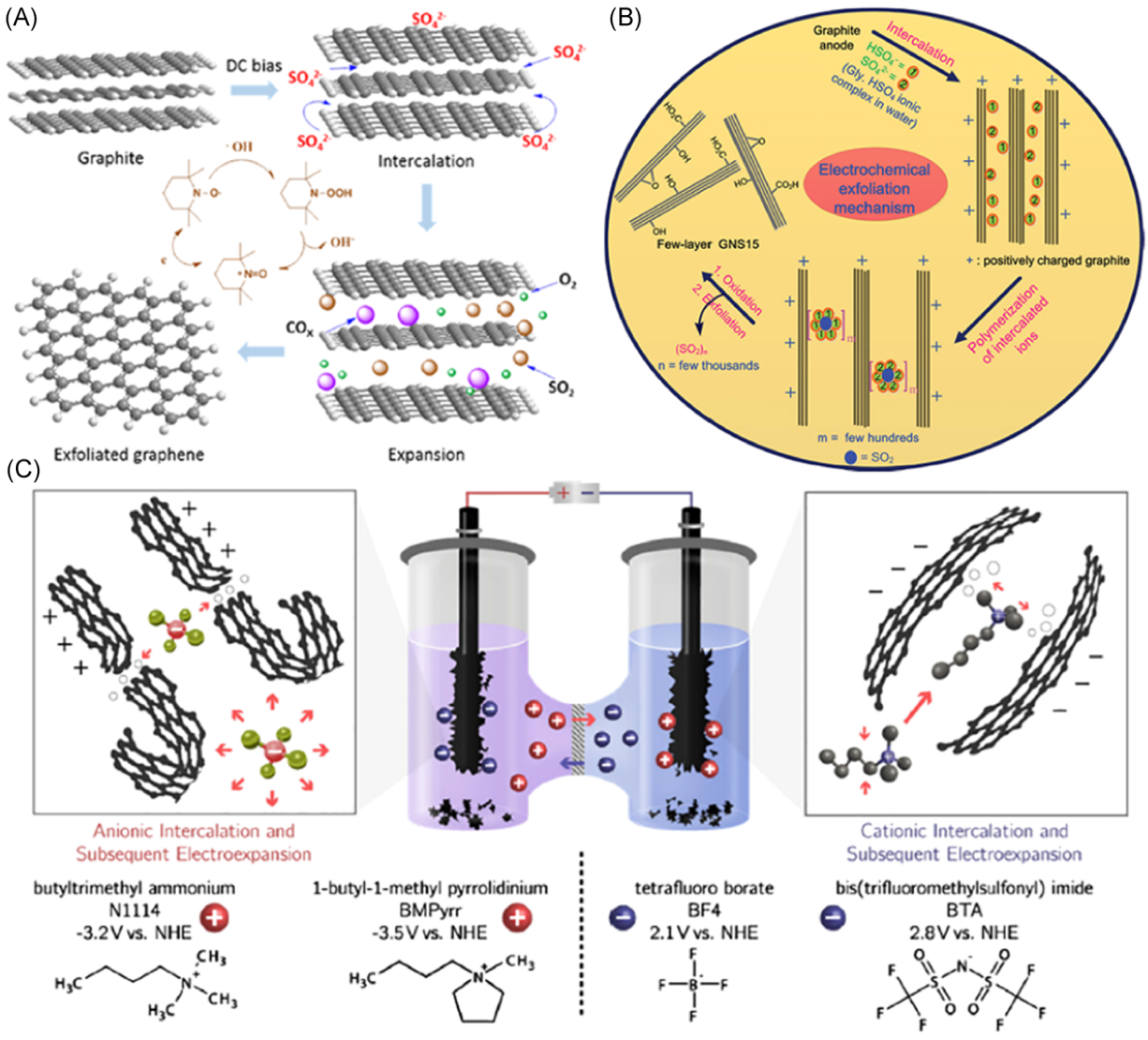

FIGURE 7 Schematic illustrations of (A) the role of TEMPO in eliminating hydroxyl radicals during the exfoliation of graphite in aqueous electrolyte. Reprinted with permission from Yang et al,[63] Copyright, ACS, 2015. B, The intercalation of Gly·HSO_4 ionic complexes and their role in graphite exfoliation. Reprinted with permission from Rao et al,[65] Copyright, Wiley, 2015. C, Simultaneous exfoliation of anodes and cathodes in acetonitrile containing different types of ionic liquids. Reprinted with permission from Taheri et al,[68] Copyright, Elsevier, 2014. NHE, normal hydrogen electrode; TEMPO, 2,2,6,6-tetramethylpiperidin-1-yl)oxyl

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polymerization to form large clusters. These clusters led to the formation of $(SO_2)_n$ gas bubbles which facilitate the exfoliation of graphite. At the suitable 15 wt.% concentration of Gly/H_2SO_4, graphene nanosheets with two to five layers and a C/O ratio of 8 were obtained.[65] Alternatively, Xu et al used a ternary eutectic melt containing 37.4 wt.% acetamide, 28 wt.% urea, 34.6 wt.% NH_4NO_3 as the electrolyte. This electrolyte has a high viscosity and high anionic intercalation potential and low ion migration speed. Thus, both anions and solvents were cointercalated into graphite, which yielded graphene materials of one to five layers.[66] Melamine was also used as an additive in electrolytes to high-quality graphene sheets.[67] It was proposed that NH_2 groups of melamine would actively interact with graphene surface to form a hydrophilic force normal to the graphene basal plane, which facilitated the exfoliation of graphite. Further, the as-exfoliated graphene sheets were encapsulated by the melamine molecule, preventing further oxidation. Over 80% of resulting graphene materials were less than three layers with a lower oxidation density (C/O ratio of 26.17) and low defect level ($I_D/I_G < 0.45$).

Although ILs can be used as electrolytes to produce graphene materials, their high cost limits their scalable applications. Taheri Najafabadi and Gyenge used acetonitrile as a nonreactive diluting solvent to have electrolytes with a low concentration of ILs (ie, 0.1M).[68] As illustrated in Figure 7C, several different ILs were tested for either anionic or cationic intercalation. Graphene materials with less than five layers can be synthesized with a high production yield. Deep eutectic solvents are ionic solvents formed by mixing eutectic acids and bases. There are four types of eutectic solvents, type I (quaternary ammonium salt + metal chloride), type II (quaternary ammonium salt + metal chloride hydrate), type III (quaternary ammonium salt + hydrogen bond donor), and type IV (metal chloride hydrate + hydrogen bond donor). They are environmentally friendly and cheaper alternatives for common ILs. Chakrabarti et al investigated graphene synthesis using various types of deep eutectic solvents mixed with a standard IL in acetonitrile at a ratio of 1:1:30 by volume. The highest graphene material (four to five layers) yield was obtained by using a type IV deep eutectic solvent ($ZnNO_3 \cdot 6H_2O$/urea).[69]

In summary, to avoid damages of graphene by acidic electrolytes, various salts, bases, or organic compounds have been explored as electrolytes for graphene material synthesis. Some ions or organic molecules in these electrolytes, which can react with oxidative radicals generated during graphite exfoliation, are beneficial for improving the quality of resulting graphene materials. Besides, amphiphilic anions can also be added in electrolytes to enhance the dispersion of exfoliated graphene flakes. Further, some organic compounds can be polymerized in situ among graphene sheets to facilitate the exfoliation of graphite.

2.4 | Additional reduction methods for graphene synthesis

In general, GO can be reduced to rGO in many ways to improve the quality of graphene materials. Several different reduction approaches have been coupled with electrochemical exfoliation of graphite to produce rGO materials. The most common method is thermal annealing. For example, Gurzęda et al[70] applied a simple thermal reduction at 500°C in the air on GO produced from electrochemical exfoliation of graphite in $HClO_4$ aqueous electrolyte. The C/O ratio increased from 10.1 to 19.7. Marković et al[71] made a more detailed comparison of thermal annealing of carbon films made from electrochemically exfoliated GO. The C/O ratios GO produced from graphite rods, and HOPG were 5.34 and 2.21, respectively. After thermal annealing at 800°C, the C/O ratios were increased to 13.89 and 13.47, respectively. However, the rGO sheets were restacked together after the high-temperature annealing. Alternatively, Gong et al[72] used spark plasma sintering at 1500°C to treat electrochemically exfoliated GO. Oxygen functional groups were eliminated, resulting in graphene materials with low defect density (I_D/I_G ration of 0.16) and high C/O ratio of 25.3.

Besides, Abdelkader et al proposed an in situ reduction method to reduce GO during the exfoliation of graphite. They used a quaternary ammonium-based deep eutectic solvent (urea/choline chloride ($(CH_3)_3NCH_2CH_2OH$]Cl) at the mole ratio of 2:1) with 2.5 wt.% LiCl as the electrolyte.[73] Under the applied −2.5 V potential, Li and ammonium derivatives were generated in situ on the surface of graphite cathodes, which can serve as reducing agents to hydrogenate graphite to produce hydrogenated graphene materials.

3 | GO SYNTHESIS BY ELECTROCHEMICAL EXFOLIATION

GO nanosheets are of interest due to their high solubility in various solvents, which makes them a promising precursor for scalable preparation of various graphene-based materials. Significantly oxidized graphene materials (with a C/O ratio smaller than 10) can be obtained from anodic exfoliation in electrolytes composed of IL-water mixture or acidic aqueous

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mediums by galvanostatic methods. The pretreatment of the graphite electrodes, as well as the use of oxidative electrolytes, exhibit a strong influence on the oxidation level of GO products. Meanwhile, the operation parameters, such as applied voltages, electrolyte temperatures, and mechanical forces, also play essential roles in determining the properties of the resulting graphene materials. In this section, we summarize some recently developed exfoliation approaches toward the production of GOs, and some results are tabulated in Table 2 for comparison.

3.1 | Graphite electrode pretreatment for GO synthesis

The electrochemical exfoliation of graphite is usually initiated by intercalation of ions followed by expansion induced by gaseous products. Thus, the exfoliation may be improved if more ions can be intercalated during electrode pretreatment. As illustrated in Figure 8A, this approach was demonstrated by treating graphite electrodes using concentrated H_2SO_4, in which H_2SO_4 molecules filled the inner voids and interstices of graphite foil electrodes. The GO production yield increased from 10 to 50 wt.% when graphite foils were treated up to 72 hours.[78] The resulting GO materials were less than four layers with a C/O ratio of 5. Cao et al reported an alternative pretreatment method. As shown in Figure 8B, graphite foil was first charged under 2.2 V in 95% H_2SO_4 for 10 minutes to produce H_2SO_4 intercalated graphite, which was then exfoliated using conventional anodic exfoliation method. This two-step approach led to GO material with a high yield (>70 wt. %), good quality (>90% monolayer), and a low C/O ratio of 3.2.[79] Ren et al reported a similar two-step method. Graphite paper was first intercalated in 50 wt.% H_2SO_4 under 1.6 V, followed by anodic exfoliation under 5 V. They further demonstrated that the oxidation degree of GO can be tuned by changing the concentration of H_2SO_4 and highly oxidized GO with C/O less than 2 was obtained when the concentration is in the range of 40 to 60 wt.%.[80] Alternatively, Sahoo et al[81] used a cathodic pretreatment step by applying −10 V on a graphite electrode for 30 seconds in 1M H_2SO_4. H_3O^+ ions were intercalated into graphite during the cathodic pretreatment, which enables more efficient anodic exfoliation in the second step. The resulting GO have a C/O ratio of 1.7.

3.2 | Oxidative electrolytes for GO synthesis

Oxidative electrolytes, for example, H_2SO_4, $HClO_4$, and HNO_3 are often used for GO synthesis by electrochemical exfoliation. Anions in these electrolytes can be intercalated into graphite under specific potentials. The subsequent electrochemical decomposition of interacted anions would generate various oxidative radicals (HO• and O•), which introduce O functional group on resulting GO. Further, the oxidation degree of GO can be controlled to some extent by the types and concentration of oxidative electrolytes.

An early study by Abdelkader et al showed that when 0.2M HNO_3 was added to 0.2M sodium citrate electrolyte, the C/O ratio of GO decreased significantly from 7.6 to 4. The decreased C/O ratio indicated that HNO_3 would introduce more O functional groups through highly oxidative $NO_2^{-\bullet}$ radicals generated during their electrochemical decomposition.[82] Coroş et al[83] used the strongly oxidative H_2SO_4/HNO_3 mixture at the ratio of 3:1 as electrolytes. The resulting GO has a low C/O ratio of 0.81.

Although the first chemical synthesis of GO was achieved using $KClO_4$ and fuming nitric acid dated back to 1859,[93] Gurzęda et al[84] first carried out electrochemical exfoliation of graphite in 8M $HClO_4$. The intercalated ClO_4^- anions contributed to the oxidation of graphene. The C/O ratio decreased from 18 of pristine graphite to 9.8 of resulting GO. This relative high C/O ratio may be contributed to the low potential (1.4 V) used in this study. Sahoo and Mallik[85] further investigated the dependence of the physicochemical properties of the exfoliated GO on the concentration of $HClO_4$ electrolytes.[85] The oxidation level in GO increased with the increase of $HClO_4$ concentration from 0.5M to 2M. The three- to six-layered GO sheets have a low C/O ratio of 1.6. Alternatively, Ambrosi and Pumera[86] used 0.5M $LiClO_4$ as electrolytes in comparison with 0.5M H_2SO_4 or Na_2SO_4. $LiClO_4$ produced GO with the lowest C/O ratio of 4.0 among the three electrolytes. It was proposed that ClO_4^- introduced oxygenated functional groups and fewer structural defects compared with SO_4^{2-}, as supported by a lower Raman I_D/I_G ratio of 1.0 vs 1.34 of GO synthesized using H_2SO_4 electrolyte.

Several other oxidizing materials, such as Na_2WO_4, $NaNO_3$, and H_2O_2 have also been explored as electrolytes for GO synthesis.[87,88] H_2O_2 was found to introduce many defects to graphene materials. $NaNO_3$ produced GO materials with a substantial thickness of 50 nm, suggesting a poor exfoliation capability. Tian et al reported the use of Oxone (potassium monopersulfate, $KHSO_5{\cdot}0.5\ KHSO_4{\cdot}K_2SO_4$) solution, which has a stronger oxidizing capacity than other commonly used electrolytes. Combined with a high voltage at 50 V, GO with a high O content (C/O ratio, 5.1) was obtained.[89]

In summary, pretreatment of graphite electrodes to intercalate ions, using strong oxidative electrolytes

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TABLE 2 A summary of recent representative studies on the synthesis of graphene oxide materials by electrochemical exfoliation of graphite

Electrolytes	Graphite electrodes	Power supplies	Additional conditions	Properties of graphene materials				References
				C/O ratios	Lateral size (μm)	No. of layers	I_D/I_G	
0.1M K_2SO_4	Graphite foil	Anodic, +10 V, DC	Concentrated H_2SO_4	5	0.5-1	<4	NA	[78]
0.1M $(NH_4)_2SO_4$	Graphite foil	Anodic, +10 V, DC	Galvanostatic charging at 2.2 V in H_2SO_4	4.6	3.1	1	1.48	[79]
50 wt.% H_2SO_4	Graphite paper	Anodic, +5 V, DC	At 1.6 V in 98 wt.% H_2SO_4	1.5-1.8	1-10	1-3	NA	[80]
1M H_2SO_4	Graphite sheet	Anodic, +8 V, DC	Cathodic pretreatment in H_2SO_4	1.7	0.1-0.12	3-5	1.1	[81]
0.2M sodium citrate	Graphite flake	Anodic, +0.3 mA, DC	0.2M HNO_3	7.6 or 4	NA	1.1 nm	NA	[82]
1M H_2SO_4/HNO_3 (3:1)	Graphite rods	Anodic, +3 V, DC	0.5M-3M, 2-10 V	0.35	NA	2	0.81	[83]
8M $HClO_4$	Graphite flake	Anodic, +1.4 V, DC	LSV	9.8	NA	NA	0.75	[84]
2M $HClO_4$	Graphite sheet	Anodic, +8 V, DC	0.5M-2M	1.6	0.1	3-6	1.04	[85]
0.5M $LiClO_4$	Graphite foil	Anodic, +10 V, DC	H_2SO_4, Na_2SO_4	4	3-10	6-8	1	[86]
0.1M Na_2WO_4	Graphite rod	Anodic, +10 V, DC		NA	1	<9	<1	[87]
0.1M SDBS, 1.5M $NaNO_3$, 1M H_2O_2	Graphite rod	Anodic, +10 V, DC	0.1M-2M, H_2SO_4, HNO_3	NA	NA	50, 20 nm	0.73, 1.02	[88]
0.05M Oxone	Graphite foil	Anodic, +50 V, DC		5.1	1-5	2-5	1.24	[89]
0.1M $(NH_4)_2SO_4$	Graphite rods	Anodic, +10 V, DC	25°C-95°C, H_2O_2	5.6	NA	2	0.32	[90]
2M H_2SO_4	Graphite plate	Anodic, +5 V, DC	27°C-60°C	NA	NA	2-6	0.25	[91]
1M H_2SO_4, $(NH_4)_2SO_4$	Graphite flakes	Anodic, 0.6 A, DC	Stirring up to 1200 rpm	3.6	1-10	1-2	1	[92]

Abbreviations: LSV, linear sweep voltammetry; Oxone, potassium monopersulfate, $KHSO_5{\cdot}0.5\ KHSO_4{\cdot}K_2SO_4$; SDBS, sodium dodecylbenzenesulfonate.

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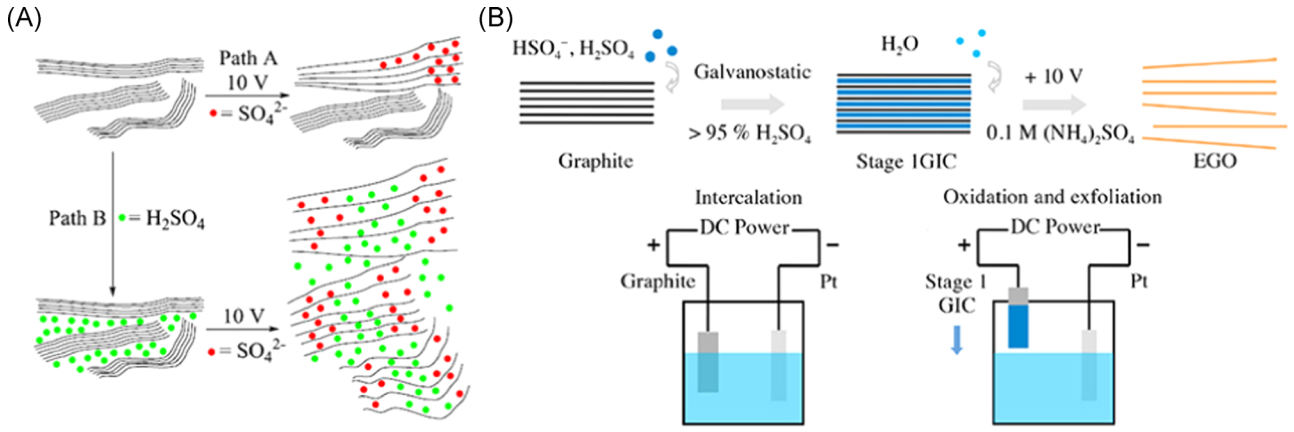

FIGURE 8 A, Schematic illustration of the anodic exfoliation of graphite foil without and with the pretreatment by H_2SO_4. Reprinted with permission from Munuera et al,[78] Copyright, Elsevier, 2017. B, Schematic illustration of the two-step electrochemical intercalation and exfoliation method to produce GO. Reprinted with permission from Cao et al,[79] Copyright, ACS, 2017. EGO, electrogenerated graphitic oxide; GIC, graphite intercalation compound

or adding other oxidizing materials are beneficial for the efficient synthesis of GO materials. Depending on the end-use of GO materials, these parameters should be tailored to yield GO with desirable properties.

3.3 | Operation parameters for GO synthesis

As illustrated in Figure 9, Zhang et al[94] studied the anodic oxidation of graphite in aqueous $NaNO_3$ electrolyte and provided some useful insights into

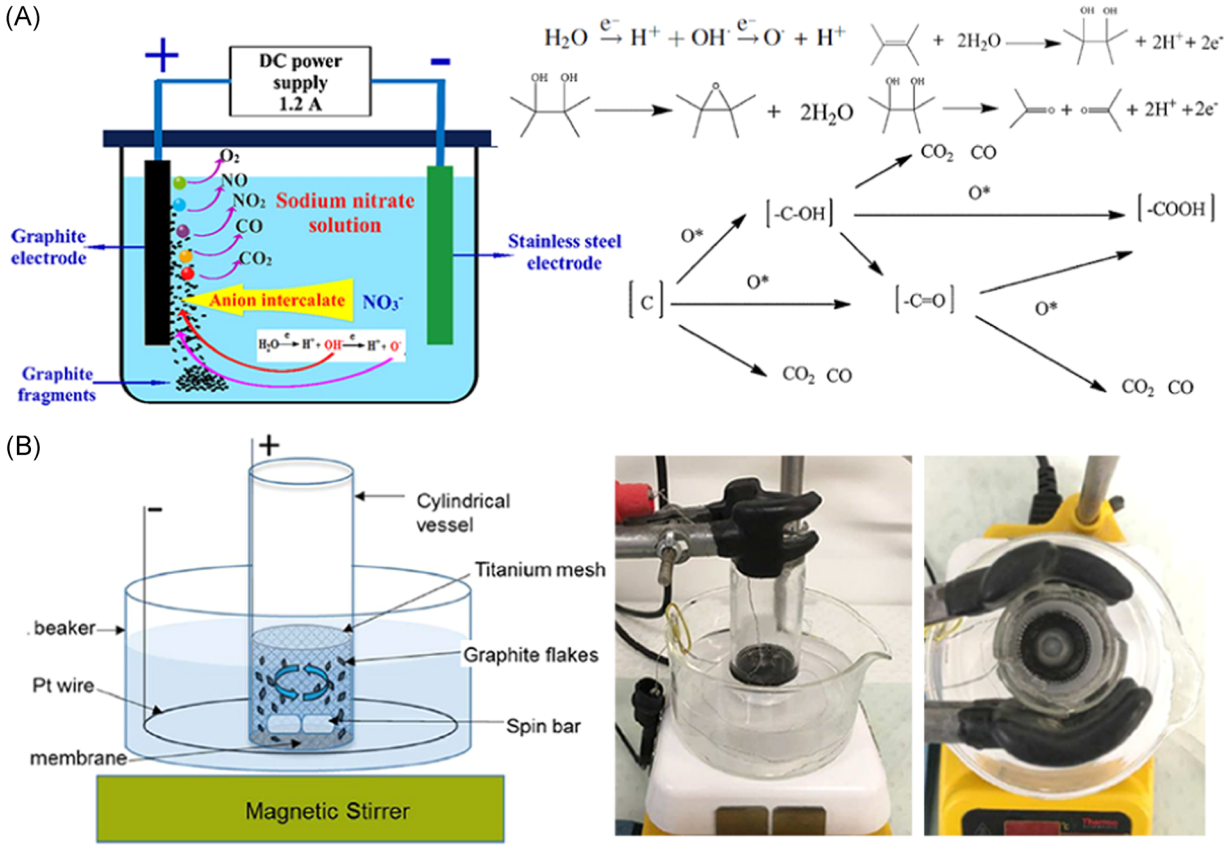

FIGURE 9 A, Schematic illustration of the experiential setup and the reaction mechanism for anodic oxidation of graphite in aqueous $NaNO_3$ electrolyte. Reprinted with permission from Zhang et al,[94] Copyright, Springer, 2016. B, Schematic drawing and a photo of the experimental setup used to include mechanical forces during GO synthesis. Reprinted with permission from Yu et al,[92] Copyright, ACS, 2016. GO, graphene oxide

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electrochemical exfoliation of graphite. First, the applied voltage bias would split water to produce radicals. Next, these radicals attack sp^2 carbon atoms at the edges and defects of graphite electrodes first to generate hydroxyl groups. Later, more hydroxyl groups would be created at both basal planes and edges of graphite. Hydroxyl groups on the basal planes can be condensed into epoxy groups, while those at the edges can be oxidized into carbonyl groups. Ketone groups at the edges can also be further oxidized into carboxyl groups. The graphite exfoliation could be attributed to the interplay of water electrolysis, anionic intercalation, and gas evolution. Further, the mechanical force caused by gas eruptions was identified as the most critical factor to disintegrate graphite electrodes.[94] On the basis of these oxidation steps, other than electrodes and electrolytes, and the oxidation degree of GO would strongly depend on the various operation parameters, such as applied potentials, temperature, and mechanical forces. These parameters can be used to tailor the quality and production yield of GO.

First, increasing the exfoliation voltage allows faster production of HO• and O• radicals, which would create GO with more functional groups and structural defects. For example, Tian et al used the 50 V to produce GO composed of two to five monolayers.[89] This GO material has a good water solubility (1.04 g/L), which can be further concentrated to produce a viscous slurry with a concentration as high as 30.5 g/L. The high voltage can also be used to create small GO quantum dots. The high oxidation degree of such GO quantum dots improves their solubility, leading to enhanced photoluminescence yield for some potential imaging applications.[95,96]

Second, the exfoliation temperature may change the generation of oxidative radicals and their reactions with graphite, leading to different sometimes contradictory exfoliation conditions. In one study, Hossain and Wang[90] varied temperatures from 25°C to 95°C with the addition of H_2O_2 in 0.1M $(NH_4)_2SO_4$ electrolyte. They found that the edge defects or O functional groups decrease with the increase of exfoliation temperature. In another study, graphite was exfoliated in 2M H_2SO_4 from 27°C to 60°C.[91] The oxidation level of GO increases with the increase of temperature. The differences between these two studies may be related to different electrolytes they used. They offered the possibility of tuning the properties of GO by controlling the operation temperature.

Third, mechanical forces can be applied to facilitate the exfoliation. As shown in Figure 9B, Yu et al[92] designed an apparatus to produce GO from graphite flakes.[92] Graphite flakes were placed inside a cylindrical glass tube. The bottom of the tube was capped with a polyvinylidene fluoride membrane. Metal oxide coated Ti mesh was placed around the inner wall of the tube as the positive electrode, while a Pt wire was used as the negative electrode. The whole apparatus fitted on top of a magnetic stirrer, so a spin bar generated mechanical forces. Under the stirring up to 1200 rpm, one to two-layered GO with the C/O ratio of 3.63 was produced.

In summary, applying higher potentials, increasing the temperature of electrolytes, and introducing mechanical forces can facilitate the synthesis of GO materials. The challenges lie in how to precisely control these operation parameters to yield GO materials with desirable properties.

4 | GRAPHENE COMPOSITE SYNTHESIS BY ELECTROCHEMICAL EXFOLIATION

Pristine graphene has a zero-band gap and is inert to many chemical reactions. Doping graphene with heteroatoms, such as N, P, and S can significantly change its electronic and catalytic properties.[97,98] Different organic or inorganic molecules can also be grafted or anchored on graphene through covalent bonds or intermolecular interactions, such as electrostatic and the van der Waals forces. The addition of these molecules brings attractive new properties for many potential applications.[99,100] It is also desirable to develop one-pot synthesis methods to achieve graphene material synthesis and functionalization simultaneously. Further, researchers have also using electrochemical exfoliation methods to control the assembly of graphene materials. Table 3 summarizes some of the representative studies. In the following four subsections, we discuss recent studies related to doping graphene materials, covalent functional, incorporation of nanoparticles, and assembly of graphene composites, respectively.

4.1 | Heteroatom doping during electrochemical exfoliation

Heteroatom doping of graphene can be achieved simultaneously during the electrochemical exfoliation of graphite under ambient conditions or by chemical functionalizing electrochemically exfoliated graphene materials in solvents. Both approaches have some advantages over other doping methods, such as thermal annealing/condensation, and solvothermal reactions, which would require much harsher reaction conditions. In recent studies, the doping of F, N, P, and S into electrochemically exfoliated graphene have been demonstrated.

Doping F into graphene has been used to improve the solution processability of graphene materials.[101] For

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TABLE 3 A summary of recent representative studies on the synthesis of graphene composites by electrochemical exfoliation of graphite

Electrolytes	Graphite electrodes	Power supplies	Additional conditions	Properties of graphene materials				References
				C/O ratio/dopant concentration (at.%)	Lateral size (μm)	No. of layers	I_D/I_G	
0.1M $NaBF_4$	Graphite foil	Anodic, +10 V, DC		4.1/3(F)	3-12	<3	1.25	[101]
Urea choline chloride/water	Graphite rod	Anodic, +5 V, DC	NaF/H_2SO_4	NA	NA	NA	>1	[102]
0.5M H_2SO_4	Graphite rod	Anodic, +6 V, DC	Urea	6.1/0.43(N)	NA	40-80	0.5	[103]
2M NaOH, 2M NH_4OH	Graphite rod	Cathodic, −60 V, DC	NH_4OH	11.1/0.71(N)	1	4	0.79	[104]
1M NaN_3	Graphite rod	Anodic, +4 V, 0.02 Hz	Pulse mode	17/0.6(N)	0.2-0.5	7-9	NA	[105]
3M glycine/25% ammonia	HOPG	Anodic, +10 V, DC		3.2/6.05(N)	NA	NA	1.5	[106]
10 wt.% $(NH_4)_2HPO_4$	HOPG	Anodic, +5 V, DC	$(NH_4)_2SO_4$, NH_4NO_3	3.6/8.4(N)	N.A	NA	NA	[107]
2M H_3PO_4	Graphite rod	Anodic, +5 V, DC		14.9/0.68(P)	0.05-0.07	3-4	0.95	[108]
0.1M phytic acid	Graphite foil	Anodic, +10 V, DC	PLA/Fe composites	14.8/0.84(P)	5-20	4	0.35	[109]
$Na_2S_2O_3/H_2SO_4$ (3:1)	Graphite rod	Anodic, +5 V, DC		5.9/3.47(S)	NA	2-3	0.92	[110]
0.1M $CsClO_4$, 1 mM NBD/BBD, DMSO	Graphite foil	Cathodic, −4 V, DC	3-Electrode, chronoamperometry	NA/4.8(N), 5.2(Br)	0.5-3.5	2.4-20 nm	2, 3	[111]
0.1M H_2SO_4, AQ diazonium ions	Graphite foil	Anodic, +10 V, DC		7.7	NA	1-4	0.11	[112]
0.1M Na_2SnO_3	Graphite rod	Anodic, +10 V, DC	Na_2SnO_3	10.9/2.4(Sn)	2-10	1-2	0.98	[113]
0.47M H_2SO_4	Graphite flakes	Anodic, +30 V, DC	Pulse, $FeCl_3$ intercalation	NA/25(Fe)20(Cl)	NA	NA	low	[114]
0.5M H_2SO_4	Graphite rod	Anodic, 50 mA/cm^2, DC	Quinone, $FeSO_4$	NA/28(Fe_3O_4)	1-2	1-3	1.35	[115]
0.1M $LiClO_4$, 0.1M $TEABF_4$ in DMC/EC	Graphite foil	Cathodic, −4 V, DC	$NaAuCl_4$, $Co(NO_3)_2$	31.7/2.2(Au)	0.1-0.5	1	1.4	[116]
$[BMIM]FeCl_4$	Graphite foil	Anodic, +4 V, DC	CV (−2 to 2 V)	41.6/1.37(N),0.17(Fe)	20	<5	NA	[117]
Tetraethyl ammonium perchlorate in DMF	HOPG	Cathodic, −2.2 V, DC	Acrylonitrile	PAN(15 wt.%)	0.5-6	1-2	0.06	[118]
0.1M Na_2SO_4	Graphite rod	Anodic, +5 V, DC	$Ni(pydcH)_2$	3.5/2.5(Ni)	NA	a few	NA	[119]
0.2M KCl	Graphite rod		TPyP	NA/C:N = 39.14	NA	2	NA	[120]

(Continues)

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TABLE 3 (Continued)

Electrolytes	Graphite electrodes	Power supplies	Additional conditions	Properties of graphene materials				
				C/O ratio/dopant concentration (at.%)	Lateral size (μm)	No. of layers	I_D/I_G	References
		Anodic, +12 V, DC						
$NH_3{\cdot}H_2O$, $(NH_4)_2SO_4$	Graphite flake	Anodic, +8 V, DC	Ni foam (cathode)	NA	NA	a few	NA	121
0.1M $[Py_{1,4}][BF_4]$	Graphite rod	Anodic, +10 V, DC	MoS_2, MnO_2, g-C_3N_4 (cathode)	NA	NA	NA	0.25	122
0.5M H_2SO_4	Graphite flakes	Anodic, +10 V, DC		2.48	NA	a few	1.25	123

Abbreviations: AQ, 9,10-anthraquinone; BBD, bromobenzenediazonium tetrafluoroborate; [BMIM]$FeCl_4$, 1-butyl-3-methylimidazolium tetrachloro-ferrate; DMF, dimethylformamide; DMC, dimethyl carbonate; DMSO, dimethyl sulfoxide; EC, ethylene carbonate; HOPG, highly oriented pyrolytic graphite; NBD, nitrobenzenediazonium tetrafluoroborate; Ni(pydcH)$_2$, nickel pyridine-2,6-dicarboxylate; PAN, polyacrylonitrile; PLA, polylactic acid; $[Py_{1,4}][BF_4]$, 1-butyl-1-methylpyrrolidinium tetrafluoroborate; $TEABF_4$, tetraethyl ammonium tetrafluoroborate; TPyP, 5,10,15,20-tetra(4-pyridyl) porphyrin.

example, Wu et al used 0.1M $NaBF_4$ as a neutral electrolyte. BF_4^- anions served as the F precursor. F-doped graphene materials with 3 at.% of F were obtained, which have less than three layers and large lateral size (up to 12 μm). Alternatively, Kakaei et al[102] added NaF into 10M H_2SO_4 to functionalize electrochemically exfoliated rGO. The characterization results suggest that some F was incorporated.

Adding N-containing molecules, such as urea, ammonia, azide, and glycine in electrolytes may directly dope N into electrochemically exfoliated graphene. For example, Ilangovan et al[103] added urea in an H_2SO_4 electrolyte, and the resulting graphene materials contained a small amount of N at 0.43 at.%. As illustrated in Figure 10A, Yen et al[104] applied −60 V on a graphite cathode, which generated in situ H_2 plasma. When 2M NH_4OH was added to a 2M NaOH alkaline electrolyte, direct electron dissociation induced by the plasma discharge generated various radicals, that is, $NH_3^{\bullet}$, $NH_2^{\bullet}$, $NH^{\bullet}$. These N-containing radicals would react with electrochemically exfoliated graphene, as shown in the reactions listed in Figure 10A, resulting in N-doped graphene materials with 0.71 at.% N. Similarly, azide anions (N_3^-) in sodium azide (NaN_3) aqueous electrolytes would decompose into NH_3, which doped exfoliated graphene with N abundance of 0.6 at.%.[105] In contrast, Yang et al[106] used 3M glycine/ammonia aqueous electrolyte, in which NH_3 oxidation intermediates reacted with expanded graphite sheets, resulting in a high N doping level of 6.05 at.%. Alternatively, the 10 wt.% $(NH_4)_2HPO_4$ electrolyte produced a high concentration of NH_4^+ ions, which would take part in the in situ amino-functionalization reactions. The resulting graphene materials had a high N content with an N/C ratio of 8.4 at.%.[107]

P- or S-doped graphene materials have been used as electrocatalysts for energy conversion applications, which can also be synthesized by electrochemical exfoliation in electrolytes containing P or S compounds. For example, Thirumal et al[108] used H_3PO_4 as an electrolyte, and the resulting graphene materials have P abundance of 0.68 at.%. Slightly increased P content of 0.84 at.% was achieved by using an environmentally friendly phytic acid (0.1M) as an electrolyte.[109] When sodium thiosulfate ($Na_2S_2O_3$) was used as an electrolyte, a variety of S-containing intermediates were produced from the electrochemical oxidation of $S_2O_3^{2+}$. The resulting graphene materials contained 3.47 at.% S with sulphureted species (ie, –C–S–C–).[110]

From Table 3, it can be observed that the doping content is usually not high. The doping of heteroatoms likely only takes place at defective sites and edges of graphene during the electrochemical exfoliation of graphite. Because of the relatively mild reaction

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conditions, it is difficult to dope many heteroatoms into pristine graphene planes. In contrast, much higher doping contents could be obtained using high-temperature thermal annealing/condensation or solvothermal reactions. Thus, it is essential to choose suitable doping methods depending on the material synthesis targets.

4.2 | Aryl diazonium functionalization during electrochemical exfoliation

Diazonium chemistry can be used to graft various aryl groups sp^2-hybridized carbon materials.[124] When diazonium salts are added to electrolytes, electrochemical reduction of positively charged aryl diazonium cations generates aryl radicals. These radicals may attack graphene layers in graphite electrodes. Meanwhile, N_2 generated during diazonium reduction can facilitate the expansion and exfoliation of graphite. This simultaneous graphite exfoliation and aryl-functionalization approach have been demonstrated in several studies. The resulting graphene materials functionalized with aryl groups show excellent solubility in various solvents. For example, Ejigu et al[111] exfoliated graphite in a 0.1M $CsClO_4$/DMSO electrolyte added with nitrobenzenediazonium tetrafluoroborate (NBD) or bromobenzenediazonium tetrafluoroborate. As shown in Figure 10B, NBD can be reduced to nitrobenzene radicals, which are highly reactive toward carbon electrodes. The nitrobenzene anchored on the carbon surface is easily further reduced to a stable nitro radical or dianion species. The dianion species can be rapidly protonated in the presence of acids.[111] Ossonon et al[112] added 2-aminoanthraquinone (2-aminoAQ) in 0.1M H_2SO_4 electrolyte, electrochemically exfoliated graphene sheets spontaneously react with aryl diazonium cations ($Ar\text{-}N_2^+$), resulting in graphene materials grafted with AQ. Similarly, Mooste et al[125] also used the same method to graft AQ on graphene materials.

4.3 | Synthesis of nanoparticle/graphene hybrids during electrochemical exfoliation

Combining graphene materials with different nanoparticles creates multifunctional hybrid materials with unique optical, electronic, and catalytic properties.[126] Conventional methods of synthesizing such nanoparticle/graphene hybrids require first dispersing graphene materials in solvents followed by depositing or growth of nanoparticles on the graphene surface. Unfortunately, because of the hydrophobic nature of pristine graphene, it is difficult to disperse graphene nanosheets individually without severe stacking or aggregation. Electrochemical exfoliation methods have been explored to synthesize nanoparticle/graphene hybrids. Some studies first synthesize the high-quality few-layered graphene nanosheets by electrochemical exfoliation of graphite and then further assemble them with different nanoparticles, such as Si, Ag, Fe_3O_4, SiO_2, Pt, and CNTs.[127-130] Other studies focused on achieving graphite exfoliation and synthesis of nanoparticle/graphene hybrids simultaneously using one-pot electrochemical exfoliation methods. For example, Zhao et al carried out electrochemical exfoliation of graphite in 0.1M Na_2SnO_3 electrolyte. SnO_2 nanoparticles were uniformly anchored on graphene with the lateral size of 2 to 10 μm and the mass loading of Sn was 2.4 at.%, which were used as lithium-ion battery electrodes.[113] Hsieh et al intercalated Fe into graphite flakes in a $FeCl_3$/HCl aqueous solution. Graphene materials incorporated with Fe nanoparticles were obtained after electrochemical exfoliation in an H_2SO_4 electrolyte, which shows two times higher electrical conductivity than that of graphene materials without Fe.[114] Alternatively, Nambi et al added quinone and Fe salts in H_2SO_4 electrolytes, Fe_3O_4 nanoparticles were incorporated in quinone functionalized graphene materials. The composite was used as electrocatalysts for H_2O_2 production.[115] Ejigu et al added $NaAuCl_4$ or $Co(NO_3)_2$ in an electrolyte containing 0.1M $LiClO_4$ and 0.1M tetraethylammonium tetrafluoroborate in dimethyl carbonate/ethylene carbonate. Various Au nanostructures and Co nanoparticles were grown on graphene materials after cathodic exfoliation of graphite electrodes.[116] Wang et al exfoliated graphite electrodes in a $FeCl_4^-$ based IL at a low potential of 2 V. Atomic Fe with the loading of 0.17 at.% were incorporated into exfoliated graphene materials, which showed excellent catalytic activities for the oxygen reduction reaction.[117]

4.4 | Assembling graphene composites during electrochemical exfoliation

Other than synthesizing graphene composites containing nanoparticles, some recent studies have also explored using electrochemical exfoliation as a tool to control the assembly of graphene composites. A relatively simple approach is to add additional compounds in electrolytes so that different molecules or polymeric compounds can be assembled on exfoliated graphene materials via various forces. For example, Ouhib et al added a vinyl monomer (acrylonitrile) in tetraethylammonium perchlorate electrolyte in dimethylformamide. As illustrated in Figure 10C, under cathodic exfoliation, acrylonitrile was intercalated and electropolymerized between the graphite layers. Parts of the polyacrylonitrile (PAN) were chemisorbed on graphene. The resulting PAN/graphene composite contains graphene materials with

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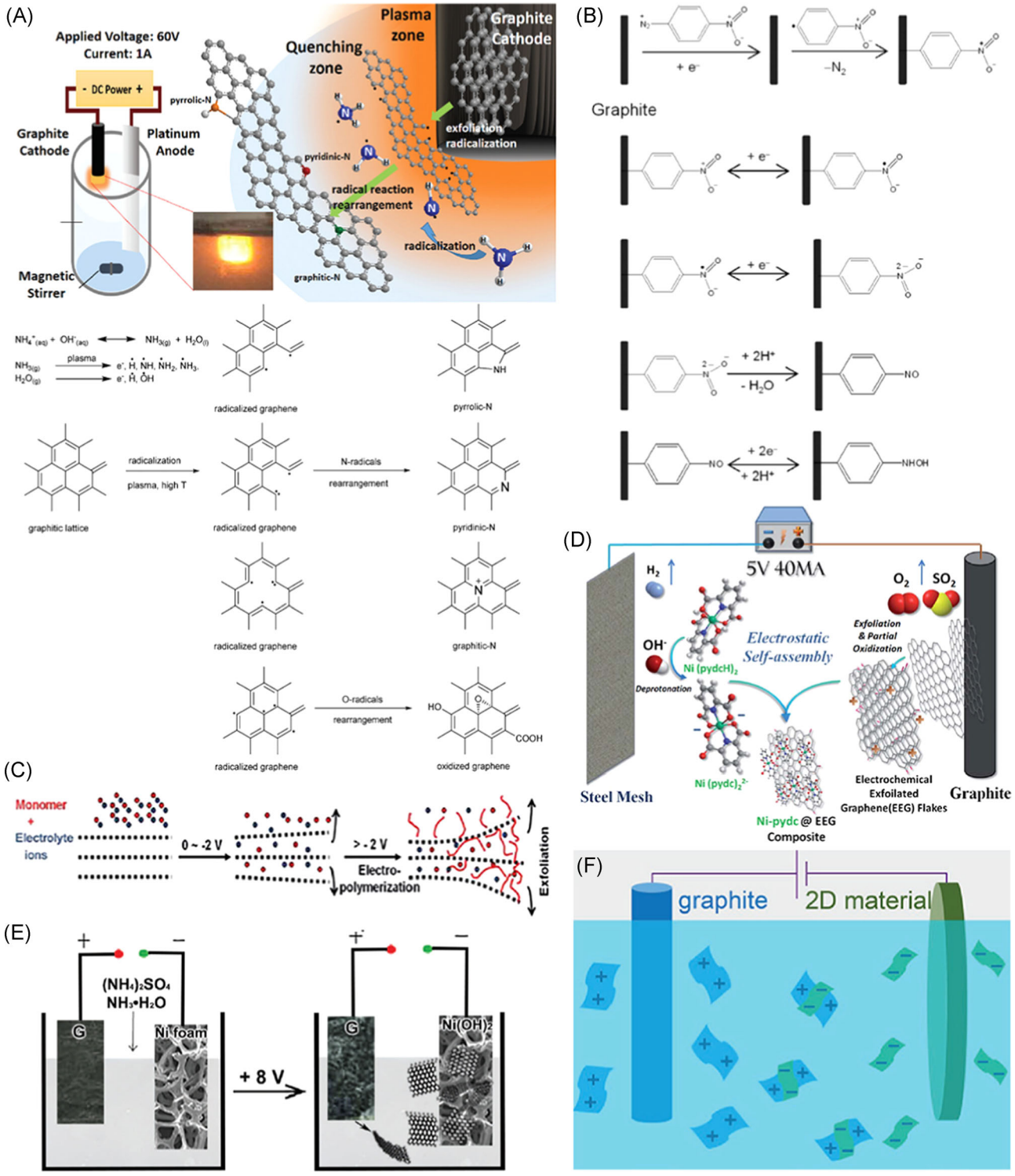

FIGURE 10 A, Schematic illustration of simultaneous graphite exfoliation and N doping and the corresponding reactions between N-containing radicals and electrochemically exfoliated graphene. Reproduced with permission from Yen et al,[104] Copyright 2017, RSC. B, Electrochemical reduction of NBD cations on a graphite electrode and the subsequent grafting and reduction steps. Reprinted with permission from Ejigu et al,[111] Copyright, ACS, 2017. C, Schematic illustration of the in situ electropolymerization of PAN among graphite layers during electrochemical exfoliation. Reproduced with permission from Ouhib et al,[118] Copyright 2014, RSC. D, Schematic illustration of the self-assembly between MOF and electrochemically exfoliated graphene. Reproduced with permission from Wang et al,[119] Copyright 2016, RSC. E, Schematic illustration of the deposition of electrochemically exfoliated graphene nanosheets on a 3D porous Ni foam electrode. Reproduced with permission from Ma et al,[121] Copyright 2016, RSC. F, Preparation of graphene-2D material composites by simultaneous electrochemical exfoliation and assembly in a single-compartment electrochemical cell. Reproduced with permission from Li et al,[122] Copyright 2018, Wiley-VCH. MOF, metal-organic framework; NBD, nitrobenzenediazonium tetrafluoroborate; PAN, polyacrylonitrile

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one to two layers and a low I_D/I_G ratio of 0.06.[118] Yang et al added hydrothermally synthesized $Ni(pydcH)_2$ (nickel pyridine-2,6-dicarboxylate) metal-organic framework (MOF) molecules in 0.1M Na_2SO_4 neutral electrolyte. As illustrated in Figure 10D, petrochemically exfoliated graphene from graphite anodes coated on deprotonated ($Ni(pydc)_2^{2-}$) via strong electrostatic interactions. The resulting MOF composites with surface coated graphene were used in asymmetric supercapacitors.[119] Maria et al exfoliated graphite in a 0.2M KCl neutral electrolyte with added 5,10,15,20-tetra(4-pyridyl) porphyrin (TPyP). TPyP was assembled on graphene by π-π stacking forming graphene/TPyP supramolecular complex, which was used in electrochemical sensors for detecting catechol.[120]

Another approach is to use porous materials as counter electrodes of graphite electrodes. Exfoliated graphene nanosheets from graphite electrodes would attach on the surface of porous counter electrodes forming 3D porous composites. For example, Ma et al[121] presented a one-step synthesis of a $Ni(OH)_2$/graphene composite via synchronous anodic exfoliation of a graphite electrode and deposition of graphene nanosheets on a 3D porous cathode. As shown in Figure 10E, $Ni(OH)_2$ was formed on the surface of 3D nickel foam, while electrochemically exfoliated graphene nanosheets were assembled on the surface of $Ni(OH)_2$. Further, as illustrated in Figure 10F, Zhang et al used a single-compartment electrochemical cell to simultaneously exfoliate anodic graphite electrodes to produce graphene materials and cathodic electrodes to produce other 2D materials, such as MoS_2, MnO_2, and graphitic carbon nitride. Due to the negative potentials applied to cathodes, the oxidation of 2D materials can be significantly suppressed. Graphene and other 2D materials were integrated together as functional composites for catalysis and supercapacitor applications.[122] Last, Chu et al utilized anodic exfoliation to create high density aligned rGO nanosheets on a graphite substrate. The graphite substrate was first exfoliated under +10 V in 0.5M H_2SO_4 at 0°C for regular intervals of 30 seconds. Due to the short time and low temperature, few-layer GO sheets with a C/O ratio of 2.48 were still attached to graphite substrates. After the further reduction in hydrazine solution, the rGO/graphite composite was used as electrodes for supercapacitors.[123]

In summary, there are mainly two approaches to assemble graphene composites during electrochemical exfoliation. One is to add additional compounds in electrolytes, so they are integrated with exfoliated graphene materials. The other is to use materials with specific structures, such as 3D porous structures, as counter electrodes, thus exfoliated graphene materials can be coated on the surface of these counter electrodes, resulting in composites with 3D structures. More studies are required to understand how these two approaches can achieve precise structure controls of composite materials.

5 | SUMMARY AND FUTURE PERSPECTIVES

The electrochemical exfoliation of graphite is emerging as an essential approach to obtaining various graphene materials. In this review, recent studies in the last 3 to 4 years indicate that the properties of graphene materials produced by electrochemical exfoliation depend on many factors, from graphite electrodes, electrolytes, various additives in electrolytes, equipment setups, power supplies to various operational parameters. We divided our discussion based on three types of graphene materials. The first type is pristine graphene materials with low defects and single layer. The second type is highly oxidized GO with excellent dispersibility. The third type is functionalized graphene and graphene composites. Although these different types of graphene materials have their specific application areas, they are all highly desirable in many potential applications.

In general, graphene synthesis requires graphite exfoliation conditions which cause fewer damages to graphene. Thus, it is desirable to exfoliate graphite electrodes quickly and avoid oxidative reactions. Thin graphite electrodes, cathodic exfoliation, low voltage, or pulse power supplies, high-temperature electrolytes, and strong mechanical forces have beneficial effects. Less-oxidative electrolytes based on salts, bases, or organic compounds may also reduce oxidative radicals generated during graphite exfoliation, leading to graphene materials with better quality. In contrast, GO synthesis would require proper pretreatment of graphite electrodes to intercalate ions, strong oxidative electrolytes, higher applied potentials, high temperature, and mechanical forces are desirable.

Despite significant research process, including several start-up companies established in recent years focusing on graphene production by electrochemical exfoliation, there are still two critical challenges. First, there is still no simple electrochemical exfoliation methods, which can precisely control the structures of resulting graphene materials. All graphene materials produced by these methods are still inhomogeneous mixtures containing different defect densities, O contents, graphene layer numbers, lateral sizes, and functional groups. Second, these methods also face the critical trade-off between the yield and the property control of graphene materials. How to synthesize graphene materials by electrochemical exfoliation targeting specific applications cost-efficiently remains an open question.

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To move forward, we propose that future research should focus on the following three areas. First, we need a better understanding of graphite exfoliation reaction mechanisms to be able to gain better structural control of resulting graphene materials. Although many studies have studied the roles of different radicals on graphite intercalation and their reactions with graphite materials, the specific reaction pathways, and reaction kinetics are still mostly missing. Second, most of the current studies are limited to small scale lab equipment setup. Large scale material production involves complex fluid mixing, heat management, and mass transport. Studies on heat and mass transport phenomena during electrochemical exfoliation are essential for efficient equipment design and process optimization. Third, various emerging applications require graphene materials with unique features. For example, membrane applications need graphene materials with tailored size, interlayer spacing, and porosity. Catalyst applications require graphene materials with suitable doping at specific reactive sites. It is unlikely that one synthesis method can produce graphene materials to meet all these diverse needs. It is crucial to develop novel electrochemical exfoliation approaches which can create graphene materials with unique features. Overall, we believe that electrochemical exfoliation will play more critical roles in the synthesis of graphene materials. Many exciting challenges are still waiting to be explored.

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CONFLICT OF INTERESTS

The authors declare that there are no conflict of interests.

ORCID

Yuan Chen http://orcid.org/0000-0001-9059-3839

REFERENCES

1. Novoselov KS, Geim AK, Morozov SV, et al. Electric field effect in atomically thin carbon films. *Science*. 2004;306:666-669.
2. Geim AK. Graphene: status and prospects. *Science*. 2009;324:1530-1534.
3. Allen MJ, Tung VC, Kaner RB. Honeycomb carbon: a review of graphene. *Chem Rev*. 2010;110:132-145.
4. Raccichini R, Varzi A, Passerini S, Scrosati B. The role of graphene for electrochemical energy storage. *Nat Mater*. 2015;14:271-279.
5. Novoselov KS, Fal'ko VI, Colombo L, Gellert PR, Schwab MG, Kim K. A roadmap for graphene. *Nature*. 2012;490:192-200.
6. Müllen K. Evolution of graphene molecules: structural and functional complexity as driving forces behind nanoscience. *ACS Nano*. 2014;8:6531-6541.
7. Narita A, Wang XY, Feng XL, Mullen K. New advances in nanographene chemistry. *Chem Soc Rev*. 2015;44:6616.
8. Zhu Y, Murali S, Cai W, et al. Graphene and graphene oxide: synthesis, properties, and applications. *Adv Mater*. 2010;22:3906-3924.
9. Batzill M. The surface science of graphene: metal interfaces, CVD synthesis, nanoribbons, chemical modifications, and defects. *Surf Sci Rep*. 2012;67:83.
10. Yang W, Chen G, Shi Z, et al. Epitaxial growth of single-domain graphene on hexagonal boron nitride. *Nat Mater*. 2013;12:792-797.
11. Sun J, Chen Y, Priydarshi MK, et al. Graphene glass from direct CVD routes: production and applications. *Adv Mater*. 2016;28:10333.
12. Emtsev KV, Bostwick A, Horn K, et al. Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide. *Nat Mater*. 2009;8:203-207.
13. Mishra N, Boeckl J, Motta N, Iacopi F. Graphene growth on silicon carbide: a review. *Phys Status Solidi A*. 2016;213:2277-2289.
14. Jiao LY, Wang XR, Diankov G, Wang HL, Dai HJ. Facile synthesis of high-quality graphene nanoribbons. *Nat Nanotechnol*. 2010;5:321-325.
15. Cai M, Thorpe D, Adamson DH, Schniepp HC. Methods of graphite exfoliation. *J Mater Chem*. 2012;22:24992.
16. Ciesielski A, Samorì P. Grapheneviasonication assisted liquid-phase exfoliation. *Chem Soc Rev*. 2014;43:381-398.
17. Parviz D, Irin F, Shah SA, Das S, Sweeney CB, Green MJ. Challenges in liquid-phase exfoliation, processing, and assembly of pristine graphene. *Adv Mater*. 2016;28:8796-8818.
18. Gayathri S, Jayabal P, Kottaisamy M, Ramakrishnan V. Synthesis of few layer graphene by direct exfoliation of graphite and a Raman spectroscopic study. *AIP Adv*. 2014;4:027116.
19. Nicolosi V, Chhowalla M, Kanatzidis MG, Strano MS, Coleman JN. Liquid exfoliation of layered materials. *Science*. 2013;340:1226419.
20. Xu Y, Cao H, Xue Y, Li B, Cai W. Liquid-phase exfoliation of graphene: an overview on exfoliation media, techniques, and challenges. *Nanomaterials*. 2018;8:942.
21. Chua CK, Pumera M. Chemical reduction of graphene oxide: a synthetic chemistry viewpoint. *Chem Soc Rev*. 2014;43:291-312.
22. Kovtyukhova NI, Ollivier PJ, Martin BR, et al. Layer-by-layer assembly of ultrathin composite films from micron-sized graphite oxide sheets and polycations. *Chem Mater*. 1999;11:771-778.

26379368, 2019, 2, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/cey2.14, Wiley Online Library on [28/07/2026]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

23. Hernandez Y, Nicolosi V, Lotya M, et al. High-yield production of graphene by liquid-phase exfoliation of graphite. *Nat Nanotechnol*. 2008;3:563-568.
24. Ciesielski A, Samorì P. Grapheneviasonication assisted liquid-phase exfoliation. *Chem Soc Rev*. 2014;43:381-398.
25. Lin L, Peng H, Liu Z. Synthesis challenges for graphene industry. *Nat Mater*. 2019;18:520-524.
26. Pei S, Cheng H-M. The reduction of graphene oxide. *Carbon*. 2012;50:3210.
27. Gao W. *Graphene Oxide*. 61. Cham, Germany: Springer; 2015.
28. Kauling AP, Seefeldt AT, Pisoni DP, et al. The worldwide graphene flake production. *Adv Mater*. 2018;30(44):e1803784.
29. Kovtun A, Treossi E, Mirotta N, et al. Benchmarking of graphene-based materials: real commercial products versus ideal graphene. *2D Mater*. 2019;6(2):025006.
30. Su C-Y, Lu A-Y, Xu Y, Chen F-R, Khlobystov AN, Li L-J. High-quality thin graphene films from fast electrochemical exfoliation. *ACS Nano*. 2011;5:2332-2339.
31. Abdelkader AM, Cooper AJ, Dryfe RAW, Kinloch IA. How to get between the sheets: a review of recent works on the electrochemical exfoliation of graphene materials from bulk graphite. *Nanoscale*. 2015;7:6944-6956.
32. Wei D, Grande L, Chundi V, et al. Graphene from electrochemical exfoliation and its direct applications in enhanced energy storage devices. *Chem Commun*. 2012;48:1239-1241.
33. Low CTJ, Walsh FC, Chakrabarti MH, Hashim MA, Hussain MA. Electrochemical approaches to the production of graphene flakes and their potential applications. *Carbon*. 2013;54:1-21.
34. Yang S, Lohe MR, Müllen K, Feng X. New-generation graphene from electrochemical approaches: production and applications. *Adv Mater*. 2016;28:6213-6221.
35. Yu P, Lowe SE, Simon GP, Zhong YL. Electrochemical exfoliation of graphite and production of functional graphene. *Curr Opin Colloid Interface Sci*. 2015;20:329-338.
36. Paredes JI, Munuera JM. Recent advances and energy-related applications of high quality/chemically doped graphenes obtained by electrochemical exfoliation methods. *J Mater Chem A*. 2017;5:7228-7242.
37. Choucair M, Thordarson P, Stride JA. Gram-scale production of graphene based on solvothermal synthesis and sonication. *Nat Nanotechnol*. 2009;4:30-33.
38. Ambrosi A, Chua CK, Bonanni A, Pumera M. Electrochemistry of graphene and related materials. *Chem Rev*. 2014;114:7150-7188.
39. Munuera JM, Paredes JI, Villar-Rodil S, et al. High quality, low oxygen content and biocompatible graphene nanosheets obtained by anodic exfoliation of different graphite types. *Carbon*. 2015;94:729-739.
40. Sevilla M, Ferrero GA, Fuertes AB. Aqueous dispersions of graphene from electrochemically exfoliated graphite. *Chem Eur J*. 2016;22:17351-17358.
41. Wu L, Li W, Li P, et al. Powder, paper and foam of few-layer graphene prepared in high yield by electrochemical intercalation exfoliation of expanded graphite. *Small*. 2014;10:1421-1429.
42. Achee TC, Sun W, Hope JT, et al. High-yield scalable graphene nanosheet production from compressed graphite using electrochemical exfoliation. *Sci Rep*. 2018;8:14525.
43. Chen K, Xue D, Komarneni S. Nanoclay assisted electrochemical exfoliation of pencil core to high conductive graphene thin-film electrode. *J Colloid Interface Sci*. 2017;487:156-161.
44. Huang X, Li S, Qi Z, Zhang W, Ye W, Fang Y. Low defect concentration few-layer graphene using a two-step electrochemical exfoliation. *Nanotechnology*. 2015;26:105602.
45. Mir A, Shukla A. Bilayer-rich graphene suspension from electrochemical exfoliation of graphite. *Mater Des*. 2018;156:62-70.
46. Yang S, Ricciardulli AG, Liu S, et al. Ultrafast delamination of graphite into high-quality graphene using alternating currents. *Angew Chem*. 2017;56:6669-6675.
47. Li L, Wang M, Guo J, et al. Regulation of radicals from electrochemical exfoliation of a double-graphite electrode to fabricate high-quality graphene. *J Mater Chem C*. 2018;6:6257-6263.
48. Kumar MK P, Shanthini S, Srivastava C. Electrochemical exfoliation of graphite for producing graphene using saccharin. *RSC Adv*. 2015;5:53865-53869.
49. Eredia M, Bertolazzi S, Leydecker T, et al. Morphology and electronic properties of electrochemically exfoliated graphene. *J Phys Chem Lett*. 2017;8:3347-3355.
50. Kurys YI, Ustavytska OO, Koshechko VG, Pokhodenko VD. Structure and electrochemical properties of multilayer graphene prepared by electrochemical exfoliation of graphite in the presence of benzoate ions. *RSC Adv*. 2016;6:36050-36057.
51. Tripathi P, Prakash Patel CR, Dixit A, et al. High yield synthesis of electrolyte heating assisted electrochemically exfoliated graphene for electromagnetic interference shielding applications. *RSC Adv*. 2015;5:19074-19081.
52. Zhou Q, Lu Y, Xu H. High-yield production of high-quality graphene by novel electrochemical exfoliation at air-electrolyte interface. *Mater Lett*. 2019;235:153-156.
53. Shinde DB, Brenker J, Easton CD, Tabor RF, Neild A, Majumder M. Shear assisted electrochemical exfoliation of graphite to graphene. *Langmuir*. 2016;32:3552-3559.
54. Parvez K, Wu ZS, Li R, et al. Exfoliation of graphite into graphene in aqueous solutions of inorganic salts. *J Am Chem Soc*. 2014;136:6083-6091.
55. Miao F, Majee S, Song M, Zhao J, Zhang S-L, Zhang Z-B. Inkjet printing of electrochemically-exfoliated graphene nanoplatelets. *Synth Met*. 2016;220:318-322.
56. Munuera JM, Paredes JI, Enterría M, et al. Electrochemical exfoliation of graphite in aqueous sodium halide electrolytes toward low oxygen content graphene for energy and environmental applications. *ACS Appl Mater Interfaces*. 2017;9:24085-24099.
57. Munuera JM, Paredes JI, Villar-Rodil S, Castro-Muñiz A, Martínez-Alonso A, Tascón JMD. High quality, low-oxidized graphene via anodic exfoliation with table salt as an efficient oxidation-preventing co-electrolyte for water/oil remediation and capacitive energy storage applications. *Appl Mater Today*. 2018;11:246-254.
58. Ejigu A, Fujisawa K, Spencer BF, et al. On the role of transition metal salts during electrochemical exfoliation of graphite: antioxidants or metal oxide decorators for energy storage applications. *Adv Funct Mater*. 2018;28:1804357.
59. Munuera JM, Paredes JI, Villar-Rodil S, Ayán-Varela M, Martínez-Alonso A, Tascón JMD. Electrolytic exfoliation of

26379368, 2019, 2, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/cey2.14, Wiley Online Library on [28/07/2026]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

graphite in water with multifunctional electrolytes: en route towards high quality, oxide-free graphene flakes. *Nanoscale*. 2016;8:2982-2998.
60. Parveen N, Ansari MO, Cho MH. Simple route for gram synthesis of less defective few layered graphene and its electrochemical performance. *RSC Adv*. 2015;5:44920-44927.
61. Chuang C-H, Su C-Y, Hsu K-T, et al. A green, simple and cost-effective approach to synthesize high quality graphene by electrochemical exfoliation via process optimization. *RSC Adv*. 2015;5:54762-54768.
62. Jung SM, Mafra DL, Lin CT, Jung HY, Kong J. Controlled porous structures of graphene aerogels and their effect on supercapacitor performance. *Nanoscale*. 2015;7:4386-4393.
63. Yang S, Brüller S, Wu ZS, et al. Organic radical-assisted electrochemical exfoliation for the scalable production of high-quality graphene. *J Am Chem Soc*. 2015;137:13927-13932.
64. Cai W, Feng X, Wang B, et al. A novel strategy to simultaneously electrochemically prepare and functionalize graphene with a multifunctional flame retardant. *Chem Eng J*. 2017;316:514-524.
65. Rao KS, Sentilnathan J, Cho HW, Wu JJ, Yoshimura M. Soft processing of graphene nanosheets by glycine-bisulfate ionic-complex-assisted electrochemical exfoliation of graphite for reduction catalysis. *Adv Funct Mater*. 2015;25:298-305.
66. Zhang Y, Xu Y, Zhu J, Li L, Du X, Sun X. Electrochemically exfoliated high-yield graphene in ambient temperature molten salts and its application for flexible solid-state supercapacitors. *Carbon*. 2018;127:392-403.
67. Chen CH, Yang SW, Chuang MC, Woon WY, Su CY. Towards the continuous production of high crystallinity graphene via electrochemical exfoliation with molecular in situ encapsulation. *Nanoscale*. 2015;7:15362-15373.
68. Taheri Najafabadi A, Gyenge E. Synergistic production of graphene microsheets by simultaneous anodic and cathodic electro-exfoliation of graphitic electrodes in aprotic ionic liquids. *Carbon*. 2015;84:449-459.
69. Chakrabarti MH, Manan NSA, Brandon NP, et al. One-pot electrochemical gram-scale synthesis of graphene using deep eutectic solvents and acetonitrile. *Chem Eng J*. 2015;274:213-223.
70. Gurzęda B, Florczak P, Wiesner M, Kempiński M, Jurga S, Krawczyk P. Graphene material prepared by thermal reduction of the electrochemically synthesized graphite oxide. *RSC Adv*. 2016;6:63058-63063.
71. Marković ZM, Budimir MD, Kepić DP, et al. Semi-transparent, conductive thin films of electrochemical exfoliated graphene. *RSC Adv*. 2016;6:39275-39283.
72. Gong Y, Ping Y, Li D, et al. Preparation of high-quality graphene via electrochemical exfoliation & spark plasma sintering and its applications. *Appl Surf Sci*. 2017;397:213-219.
73. Abdelkader AM, Patten HV, Li Z, Chen Y, Kinloch IA. Electrochemical exfoliation of graphite in quaternary ammonium-based deep eutectic solvents: a route for the mass production of graphane. *Nanoscale*. 2015;7:11386-11392.
74. Liu J, Poh CK, Zhan D, et al. Improved synthesis of graphene flakes from the multiple electrochemical exfoliation of graphite rod. *Nano Energy*. 2013;2:377-386.
75. Liu N, Luo F, Wu H, Liu Y, Zhang C, Chen J. One-step ionic-liquid-assisted electrochemical synthesis of ionic-liquid-functionalized graphene sheets directly from graphite: ionic-liquid-assisted electrochemical synthesis of graphene. *Adv Funct Mater*. 2008;18:1518-1525.
76. Lu J, Yang J, Wang J, Lim A, Wang S, Loh KP. One-pot synthesis of fluorescent carbon nanoribbons, nanoparticles, and graphene by the exfoliation of graphite in ionic liquids. *ACS Nano*. 2009;3:2367-2375.
77. Shang NG, Papakonstantinou P, Sharma S, et al. Controllable selective exfoliation of high-quality graphene nanosheets and nanodots by ionic liquid assisted grinding. *Chem Commun*. 2012;48:1877.
78. Munuera JM, Paredes JI, Villar-Rodil S, Martínez-Alonso A, Tascón JMD. A simple strategy to improve the yield of graphene nanosheets in the anodic exfoliation of graphite foil. *Carbon*. 2017;115:625-628.
79. Cao J, He P, Mohammed MA, et al. Two-step electrochemical intercalation and oxidation of graphite for the mass production of graphene oxide. *J Am Chem Soc*. 2017;139:17446-17456.
80. Pei S, Wei Q, Huang K, Cheng HM, Ren W. Green synthesis of graphene oxide by seconds timescale water electrolytic oxidation. *Nat Commun*. 2018;9:145.
81. Sahoo SK, Ratha S, Rout CS, Mallik A. Physicochemical properties and supercapacitor behavior of electrochemically synthesized few layered graphene nanosheets. *J Solid State Electrochem*. 2016;20:3415-3428.
82. Abdelkader AM, Kinloch IA, Dryfe RAW. High-yield electro-oxidative preparation of graphene oxide. *Chem Commun*. 2014;50:8402-8404.
83. Coroş M, Pogăcean F, Roşu M-C, et al. Simple and cost-effective synthesis of graphene by electrochemical exfoliation of graphite rods. *RSC Adv*. 2016;6:2651-2661.
84. Gurzęda B, Florczak P, Kempiński M, Peplińska B, Krawczyk P, Jurga S. Synthesis of graphite oxide by electrochemical oxidation in aqueous perchloric acid. *Carbon*. 2016;100:540-545.
85. Sahoo SK, Mallik A. Synthesis and characterization of conductive few layered graphene nanosheets using an anionic electrochemical intercalation and exfoliation technique. *J Mater Chem C*. 2015;3:10870-10878.
86. Ambrosi A, Pumera M. Electrochemically exfoliated graphene and graphene oxide for energy storage and electrochemistry applications. *Chem Eur J*. 2016;22:153-159.
87. Li C, Xu Y-T, Zhao B, et al. Flexible graphene electrothermal films made from electrochemically exfoliated graphite. *J Mater Sci*. 2015;51:1043-1051.
88. Hamra AAB, Lim HN, Chee WK, Huang NM. Electro-exfoliating graphene from graphite for direct fabrication of supercapacitor. *Appl Surf Sci*. 2016;360:213-223.
89. Tian S, Yang S, Huang T, et al. One-step fast electrochemical fabrication of water-dispersible graphene. *Carbon*. 2017;111:617-621.
90. Hossain ST, Wang R. Electrochemical exfoliation of graphite: effect of temperature and hydrogen peroxide addition. *Electrochim Acta*. 2016;216:253-260.
91. Hsieh C-T, Hsueh J-H. Electrochemical exfoliation of graphene sheets from a natural graphite flask in the presence of sulfate ions at different temperatures. *RSC Adv*. 2016;6:64826-64831.
92. Yu P, Tian Z, Lowe SE, et al. Mechanically-assisted electrochemical production of graphene oxide. *Chem Mater*. 2016;28:8429-8438.

26379368, 2019, 2, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/cey2.14, Wiley Online Library on [28/07/2026]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

93. Brodie BC. XIII. On the atomic weight of graphite. *Phil Trans R Soc*. 1859;149:249-259.
94. Zhang G, Wen M, Wang S, Chen J, Wang J. Insights into electrochemical behavior and anodic oxidation processing of graphite matrix in aqueous solutions of sodium nitrate. *J Appl Electrochem*. 2016;46:1163-1176.
95. Li X, Zhao Z, Pan C. Electrochemical exfoliation of carbon dots with the narrowest full width at half maximum in their fluorescence spectra in the ultraviolet region using only water as electrolyte. *Chem Commun*. 2016;52:9406-9409.
96. Muthurasu A, Dhandapani P, Ganesh V. Facile and simultaneous synthesis of graphene quantum dots and reduced graphene oxide for bio-imaging and supercapacitor applications. *New J Chem*. 2016;40:9111-9124.
97. Rao CNR, Gopalakrishnan K, Govindaraj A. Synthesis, properties and applications of graphene doped with boron, nitrogen and other elements. *Nano Today*. 2014;9:324-343.
98. Wang X, Sun G, Routh P, Kim D-H, Huang W, Chen P. Heteroatom-doped graphene materials: syntheses, properties and applications. *Chem Soc Rev*. 2014;43:7067-7098.
99. Georgakilas V, Otyepka M, Bourlinos AB, et al. Functionalization of graphene: covalent and non-covalent approaches, derivatives and applications. *Chem Rev*. 2012;112:6156-6214.
100. Lonkar SP, Deshmukh YS, Abdala AA. Recent advances in chemical modifications of graphene. *Nano Res*. 2015;8:1039-1074.
101. Zhou F, Huang H, Xiao C, et al. Electrochemically scalable production of fluorine-modified graphene for flexible and high-energy ionogel-based microsupercapacitors. *J Am Chem Soc*. 2018;140:8198-8205.
102. Kakaei K, Balavandi A. Hierarchically porous fluorine-doped graphene nanosheets as efficient metal-free electrocatalyst for oxygen reduction in gas diffusion electrode. *J Colloid Interface Sci*. 2017;490:819-824.
103. Thirumal V, Pandurangan A, Jayakumar D, Ilangovan R. Modified solar power: electrochemical synthesis of Nitrogen doped few layer graphene for supercapacitor applications. *J Mater Sci*. 2016;27:3410-3419.
104. Yen P-J, Ting C-C, Chiu Y-C, et al. Facile production of graphene nanosheets comprising nitrogen-doping through in situ cathodic plasma formation during electrochemical exfoliation. *J Mater Chem C*. 2017;5:2597-2602.
105. Ustavytska O, Kurys Y, Koshechko V, Pokhodenko V. One-step electrochemical preparation of multilayer graphene functionalized with nitrogen. *Nanoscale Res Lett*. 2017;12:175.
106. Yang Y, Shi W, Zhang R, et al. Electrochemical exfoliation of graphite into nitrogen-doped graphene in glycine solution and its energy storage properties. *Electrochim Acta*. 2016;204:100-107.
107. Gu S-Y, Hsieh C-T, Yuan J-Y, Hsueh J-H, Gandomi YA. Amino-functionalization of graphene nanosheets by electrochemical exfoliation technique. *Diamond Relat Mater*. 2018;87:99-106.
108. Thirumal V, Pandurangan A, Jayavel R, et al. Single pot electrochemical synthesis of functionalized and phosphorus doped graphene nanosheets for supercapacitor applications. *J Mater Sci*. 2015;26:6319-6328.
109. Feng X, Wang X, Cai W, Qiu S, Hu Y, Liew KM. Studies on synthesis of electrochemically exfoliated functionalized graphene and polylactic acid/ferric phytate functionalized graphene nanocomposites as new fire hazard suppression materials. *ACS Appl Mater Interfaces*. 2016;8:25552-25562.
110. Parveen N, Ansari MO, Ansari SA, Cho MH. Simultaneous sulfur doping and exfoliation of graphene from graphite using an electrochemical method for supercapacitor electrode materials. *J Mater Chem A*. 2016;4:233-240.
111. Ejigu A, Kinloch IA, Dryfe RAW. Single stage simultaneous electrochemical exfoliation and functionalization of graphene. *ACS Appl Mater Interfaces*. 2017;9:710-721.
112. Ossonon BD, Bélanger D. Functionalization of graphene sheets by the diazonium chemistry during electrochemical exfoliation of graphite. *Carbon*. 2017;111:83-93.
113. Zhao B, Jiang L, Zeng X, et al. A highly thermally conductive electrode for lithium ion batteries. *J Mater Chem A*. 2016;4:14595-14604.
114. Hsieh YP, Chiang WY, Tsai SL, Hofmann M. Scalable production of graphene with tunable and stable doping by electrochemical intercalation and exfoliation. *Phys Chem Chem Phys*. 2016;18:339-343.
115. Divyapriya G, Nambi IM, Senthilnathan J. An innate quinone functionalized electrochemically exfoliated graphene/Fe3O4 composite electrode for the continuous generation of reactive oxygen species. *Chem Eng J*. 2017;316:964-977.
116. Ejigu A, Miller B, Kinloch IA, Dryfe RAW. Optimisation of electrolytic solvents for simultaneous electrochemical exfoliation and functionalisation of graphene with metal nanostructures. *Carbon*. 2018;128:257-266.
117. Wang J, Zhang H, Wang C, et al. Co-synthesis of atomic Fe and few-layer graphene towards superior ORR electrocatalyst. *Energy Storage Mater*. 2018;12:1-7.
118. Ouhib F, Aqil A, Thomassin J-M, et al. A facile and fast electrochemical route to produce functional few-layer graphene sheets for lithium battery anode application. *J Mater Chem A*. 2014;2:15298-15302.
119. Wang Z, Yao H, Zhang F, Li W, Yang Y, Lu X. Electro-synthesized Ni coordination supermolecular-networks-coated exfoliated graphene composite materials for high-performance asymmetric supercapacitors. *J Mater Chem A*. 2016;4:16476-16483.
120. Coroş M, Pogăcean F, Măgeruşan L, et al. Graphene-porphyrin composite synthesis through graphite exfoliation: the electrochemical sensing of catechol. *Sens Actuators B*. 2018;256:665-673.
121. Ma L, Zheng M, Liu S, et al. Synchronous exfoliation and assembly of graphene on 3D Ni(OH)2 for supercapacitors. *Chem Commun*. 2016;52:13373-13376.
122. Li F, Xue M, Zhang X, et al. Advanced composite 2D energy materials by simultaneous anodic and cathodic exfoliation. *Adv Energy Mater*. 2018;8:1702794.
123. Hu L, Peng X, Li Y, et al. Direct anodic exfoliation of graphite onto high-density aligned graphene for large capacity supercapacitors. *Nano Energy*. 2017;34:515-523.
124. Sinitskii A, Dimiev A, Corley DA, Fursina AA, Kosynkin DV, Tour JM. Kinetics of diazonium functionalization of chemically converted graphene nanoribbons. *ACS Nano*. 2010;4:1949-1954.
125. Mooste M, Kibena-Põldsepp E, Ossonon BD, Bélanger D, Tammeveski K. Oxygen reduction on graphene sheets functionalised by anthraquinone diazonium compound during electrochemical exfoliation of graphite. *Electrochim Acta*. 2018;267:246-254.

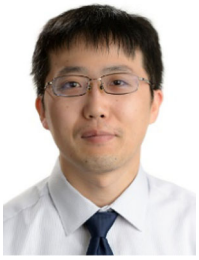
26379368, 2019, 2, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/cey2.14, Wiley Online Library on [28/07/2026]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

126. Yin PT, Shah S, Chhowalla M, Lee KB. Design, synthesis, and characterization of graphene–nanoparticle hybrid materials for bioapplications. *Chem Rev*. 2015;115:2483-2531.
127. Lopes JH, Ye S, Gostick JT, Barralet JE, Merle G. Electrocatalytic oxygen reduction performance of silver nanoparticle decorated electrochemically exfoliated graphene. *Langmuir*. 2015;31:9718-9727.
128. Wei W, Wang G, Yang S, Feng X, Müllen K. Efficient coupling of nanoparticles to electrochemically exfoliated graphene. *J Am Chem Soc*. 2015;137:5576-5581.
129. Liu Z, Wu ZS, Yang S, Dong R, Feng X, Müllen K. Ultraflexible in-plane micro-supercapacitors by direct printing of solution-processable electrochemically exfoliated graphene. *Adv Mater*. 2016;28:2217-2222.
130. Gorle DB, Kulandainathan MA. One-pot synthesis of highly efficient graphene based three-dimensional hybrids as catalyst supporting materials for electro-oxidation of liquid fuels. *J Mater Chem A*. 2017;5:15273-15286.

AUTHOR BIOGRAPHIES

Fei Liu received his PhD from Dalian University of Technology in 2012. He is currently an associate professor at Research and Development Center for Environmental Microbiology of Guangdong Institute of Microbiology. From 2017 to 2019, he was a visiting scholar at the University of Sydney working with Prof Yuan Chen. His research focuses on the design and synthesis of novel functional nanomaterials and their biological applications.

Meiying Xu is a professor and the leader of Research and Development Center for Environmental Microbiology Research in Guangdong Institute of Microbiology, Guangdong Academy of Sciences. She received her PhD in Environmental Microbiology for Graduate University of the Chinese Academy of Sciences in 2005. She worked as a visiting scholar at the University of Oklahoma, the United States from 2006 to 2008. Her research interest covers environmental microbial physiology and functional genomics, microbial ecological functions, and microbial fuel cell biological materials.



Li Wei obtained his BEng in Chemical Engineering from Tsinghua University, China, in 2006 and a PhD degree from Nanyang Technological University, Singapore in 2011. After his postdoc training, he joined The University of Sydney as a Lecturer in 2017. His research focuses on developing carbon and metal oxide-based catalysts for oxygen electrochemistry and related applications, such as water electrolysis, H_2O_2 production, and Zn-air batteries.

Yuan Chen received a bachelor's degree from Tsinghua University and a PhD from Yale University. He is a professor at The University of Sydney. His research focuses on carbon materials and their sustainable energy and environmental applications, including supercapacitors, Zn-air batteries, electrocatalysts, membranes, and antibacterial coatings. He is currently serving as an editor for *Carbon* (Elsevier). He also serves as Chair for Australian Carbon Society.

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