Carbon Letters (2021) 31:371–388
https://doi.org/10.1007/s42823-020-00212-3

Online ISSN 2233-4998
Print ISSN 1976-4251

REVIEW

# A short review on electrochemical exfoliation of graphene and graphene quantum dots

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Received: 1 September 2020 / Revised: 25 November 2020 / Accepted: 1 December 2020 / Published online: 3 January 2021

**Abstract**
The synthesis of graphene and graphene quantum dots (GQDs) employing various approaches with a range of precursors, chemicals, and parameters has been reported. Most of the top-down and bottom-up techniques employ strong and hazardous chemical environments, complicated and tedious procedures, are time-consuming, and often require special equipment. Another drawback of the techniques reported is the production of agglomerated, inhomogeneous, and non-dispersible graphene in aqueous solvents or organic solvents, thus limiting its application. This work specifically and comprehensively describes the electrochemical exfoliation of graphene and GQDs, which is often considered as a simple one-step, facile, non-hazardous, and highly efficient technique yet favourable for mass production. A brief discussion on the advantageous and challenges of the electrochemical technique and applications of the electrochemically exfoliated graphene and GQDs is also presented.

**Keywords** Electrochemical · Exfoliation · Graphene · Graphene quantum dots

## 1 Introduction

Graphene is a hexagonally arranged monolayer of two-dimensional *sp*$^2$ hybridized carbon atoms. Ever since Andre Geim and Konstantin Novoselov have successfully exfoliated the very first free-standing graphene in 2004 [1] and were awarded the Nobel Prize in Physics 2010 for “ground breaking experiments regarding the two-dimensional material graphene”, a vast amount of communities from academia, government and industry have devoted their interest in exploring graphene in terms of its properties, fabrication techniques, and potential applications [2].

Graphene is a zero band-gap semiconductor due to its partial overlapping of the valence and conduction bands [3]. The graphene structure exhibited remarkably high surface area accounting up to ~ 2630 m$^2$/g, good electrical conductivity of ~ 6000 S/cm and thermal conductivity of ~ 5000 W/m/K and strong mechanical strength with Young’s modulus up to 1 TPa and intrinsic strength of 130 GPa [4, 5]. These extraordinary properties of graphene have led to a significant number of applications such as nanofillers in polymer composite [6], anticorrosion coating for metals [7], electrochemical sensing and biosensing [8], and nanofluids as cooling agent [9].

The preparation and synthesis methods of graphene can be classified into two approaches: the top-down and bottom-up approaches. The top-down approaches commonly involve the exfoliation of graphite, the precursor through mechanical, chemical, or electrochemical processes. During the exfoliation process, the van der Waals forces between the graphite layers will be weakened to produce graphene.

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For example, the micromechanical cleavage technique (also known as the Scotch tape method) [1] is one of the simplest top-down approach to isolate a single-layer of graphene from graphite. This amazingly simple method has been able to produce the highest quality graphene crystallites when single or a few layers of graphene were transferred onto the surface of the substrate. Free-standing and high-quality graphene was produced by etching away the substrate. However, this method is low-throughput procedure, causing scientists to explore other alternative techniques. Other top-down approach such as chemical oxidation method involves strong oxidation of graphite into graphite oxide, which is then exfoliated to obtain graphene oxide sheets and finally graphene through the chemical reduction of graphene oxide. Many scientists employ this chemical route based on the principles developed by Hummers and Offeman [10] for high-throughput processing and production of graphene oxide. Hummer's method used concentrated sulphuric acid ($H_2SO_4$) and potassium permanganate ($KMnO_4$) to oxidize the graphite flakes in an ice bath. Graphene oxide obtained by the exfoliation of graphite oxide undergoes chemical reduction process using a strong reducing agent such as hydrazine hydrate to finally produce graphene sheets. Albeit the chemical technique can be applicable for high-yield production of graphene, the irreversible defects induced by heavy oxidations and extensive modifications may degrade its performance and electronic properties for certain applications.

On the other hand, bottom-up approaches assemble small molecular building blocks to produce graphene. Chemical vapour decomposition (CVD) [11], SiC decomposition [12], and organic synthesis [13] are among a few examples of bottom-up approaches [8]. The CVD technique is one of the widely known bottom-up processes which involve the thermal decomposition of hydrocarbons on transition metals. The growth of graphene through this method usually occurs under low-pressure conditions by exposure of the transition metal surface to a hydrocarbon surface [14]. High-quality graphene can be synthesized with the use of different simple-handle liquid alcohol precursors such as methanol, ethanol, and propanol on copper foils in a tube furnace via the CVD technique [14]. Although the synthesis of graphene via the CVD is scalable and viable for graphene production, the environment after the nucleating of graphene sheets, however, needs to be carefully adjusted in order to avoid the formation of grain boundaries and seeding of additional secondary layers. The bottom-up organic synthesis of graphene suffers from complicated reaction set-up and produces side reactions. All of these approaches certainly come with strengths and shortcomings depending on the nature of the graphene application.

The zero-dimensional graphene quantum dots (GQDs) are one of the newest additions to the "graphene family". The GQDs consists of graphene sheets that are less than 10 layers with dimensions less than 100 nm [15–17]. This characteristic makes GQDs very distinguishable when compared to carbon dots (CDs) in terms of its structure whereby CDs are spherically shaped and made of $sp^2$ hybridized carbon atoms with less than 15 nm in size [18]. Similar to graphene, GQDs inherit certain remarkable properties such as high electrical conductivity, excellent mechanical strength, and exceptional thermal stability. Another unique feature of GQDs is the existence of band-gap. Unlike graphene, GQDs proved to have band-gap based on previous theoretical calculations and experimental studies [19].

The GQDs have better surface grafting, excellent biocompatibility, low toxicity, chemical inertness, high photostability, stable photoluminescence, and good solubility due to edge and quantum confinement effects [18, 20]. Some of these traits make GQDs suitable to be employed in various fields including drug delivery [20], light-emitting diodes [21], energy storage [22], bioimaging, and optical sensing [23]. The application of GQDs can be further explored by functionalizing towards the desired chemical, optical or electronic properties. The GQDs can be functionalized by doping with heteroatoms, forming composites with polymers or other materials, as well as by controlling the size and shape of GQDs [19]. Doping became one of the tools in modifying GQDs properties since it was first investigated by Zhao and co-workers using nitrogen back in 2012 [24]. Besides modifications, some properties can be enhanced by co-doping with a variety of heteroatoms thus opening gates for novel properties and applications. The dopant atoms that are to be found on the inner molecules of GQDs will alter the elemental constituent, electron configuration origin, polarizability, defect amount, and structure of energy band [25].

Similar to graphene, GQDs can be synthesized by top-down and bottom-up approaches. Through both approaches, GQDs in the shape of circular or elliptical, triangular, quadrate, and hexagonal can be synthesized. Among these shapes, circular shape is the most synthesized GQDs [23, 26]. Zhang et al. [26] reported that the sizes of GQDs obtained are significantly influenced by the synthetic approach not by the raw materials. The example of top-down approaches in the synthesis of GQDs is direct cutting of graphene-like materials (such as graphite, graphene oxide, multi-walled carbon nanotubes, carbon fibres, 3D graphene, and expandable graphite) via hydrothermal or solvothermal synthesis [27, 28], acid exfoliation [29], and electrochemical exfoliation [30–35]. The advantages of following these routes are easily excess of cheap raw material (graphite), the inheritance of high graphitic structure, and the production of GQDs with oxygen-containing functional groups located at the edges which will facilitate the solubility and functionalization [2, 18]. However, these methods typically involve harsh reaction conditions, which cause damages to the graphene lattice and generate a low yield of GQDs with non-uniform size and thickness [33]. On the other hand, the examples of bottom-up approaches to synthesize GQDs from molecular precursors (natural or synthetic) are precursor pyrolysis, cyclodehydrogenation, catalysed cage opening of fullerene, thermolysis, hydrothermal fusing, and electron beam irradiation. Despite having challenging synthetic protocols, bottom-up methods offer better control of the size and shape of the GQDs production [18].

Many works have been reported on the synthesis and fabrication of graphene and GQDs using various approaches with a range of precursors, chemicals, and parameters. However, there are certain drawbacks in the fabrication methods that need to be addressed. For instance, the scotch tape method [36] is neither high throughput nor high yield. The chemical exfoliation methods [37] required the usage of strong acidic and oxidizing chemicals which intensely affect the graphitic backbone structure. In contrast, the chemical vapour deposition [38] and organic synthesis [39] required crucial control of the processing conditions. Besides requiring hazardous chemical environments, being time-consuming, and sometimes specialized equipment, both approaches often produce agglomerated, inhomogeneous and non-dispersible graphene in aqueous or organic solvents. These conditions hamper the use of graphene in many applications.

With this regard, the electrochemical route in exfoliating graphite into graphene and GQDs is preferred. The electrochemical route provides a facile, simple, and non-hazardous technique for the synthesis of graphene and GQDs. Similar in principle to that of graphite exfoliation, electrochemical synthesis of graphene generally involves the usage of graphite electrodes assisted by ionic liquids and water as the electrolyte bath. With the assistance of surfactant, homogenous and stable dispersion of graphene and GQDs suspension can be successfully synthesized. The use of a surfactant and its potential in graphene material production are practicably influenced by the interactions of ionic solutions such as sulphate, nitrate, fluoride, perchlorate, and lithium which are electrochemically involved in graphite intercalation [30]. The electrochemical method can be highlighted as simple, economical, and environmentally safe compared to other methods. Various works have been reported employing the electrochemical technique which is often considered as a one-step treatment [31, 32]. The electrochemical process is a technique that portrays the phrase old but gold. Although this technique has been established over a decade ago, it is still widely used in experimental studies and in industries until today. Electrochemical technique is mostly used in the metal industry, particularly in the production of aluminium. These techniques are also widely applied in the manufacture of peroxoacids, chlorates, and many more [2]. Herein, we report a short review on the electrochemical exfoliation of graphene and GQDs, which is facile yet favourable for mass production. We believe this review will pave the way towards the feasible and applicable large production of graphene and graphene quantum dots through various electrochemical techniques.

## 2 Electrochemical exfoliation of graphene and GQDs

### 2.1 Electrochemical exfoliation of graphene

Several works on the preparation of graphene using electrochemical exfoliation are summarized in Table 1. Htwe and co-workers [40] investigated the influence of three different types of electrolytes, namely sulphuric acid, phosphoric acid, and ammonium sulphate, with different sonication times in the electrochemical exfoliation of graphene. The graphite rod was set as the working electrode, whereas the platinum rod served as the counter electrode. The results showed that the graphene generated using sulphuric acid as the electrolyte at 45 min of sonication time was the most stable, has the smallest crystallite size, the lowest interlayer distance, high electrical conductivity and had fewer defects.

Alanyalioğlu et al. [41] reported the use of various potential value in intercalating sodium dodecyl sulphate (SDS) molecules into graphitic layers to control the thickness and the size of the graphene. The graphite was fixed as the anode, and then the electrode was switched to the cathode for the electrochemical exfoliation process to produce graphene–SDS suspensions. The mechanism of the intercalation and exfoliation process using the ionic surfactant is generally illustrated in Fig. 1. During the electrochemical process, the anionic surfactant was intercalated into the positively charged graphite anode to form surfactant-intercalated graphite (electrode) through ionic interaction, which expands the van der Waals gap between the graphite layers. Since the concentration of the SDS is above the critical micelle concentration, the formation of micelles in the solution was significant. The micelles of the surfactants interact with the graphene layers whereby the negatively charged head of the SDS attracted to the positively charged surface of the electrode. The expansion of the van der Waals gap is further promoted with the micelles formation. When the graphite anode was treated as the cathode (by changing the electric charge of the electrode), electrochemical exfoliation of the surfactant-intercalated graphite electrode occurred due to electrostatic repulsion of the anionic surfactant and negatively charged electrode. The negatively charged head of the surfactant is no longer attracted since the electric charged was changed. The exfoliation process of the surfactant–intercalated graphite results in the production of stable graphene suspension.

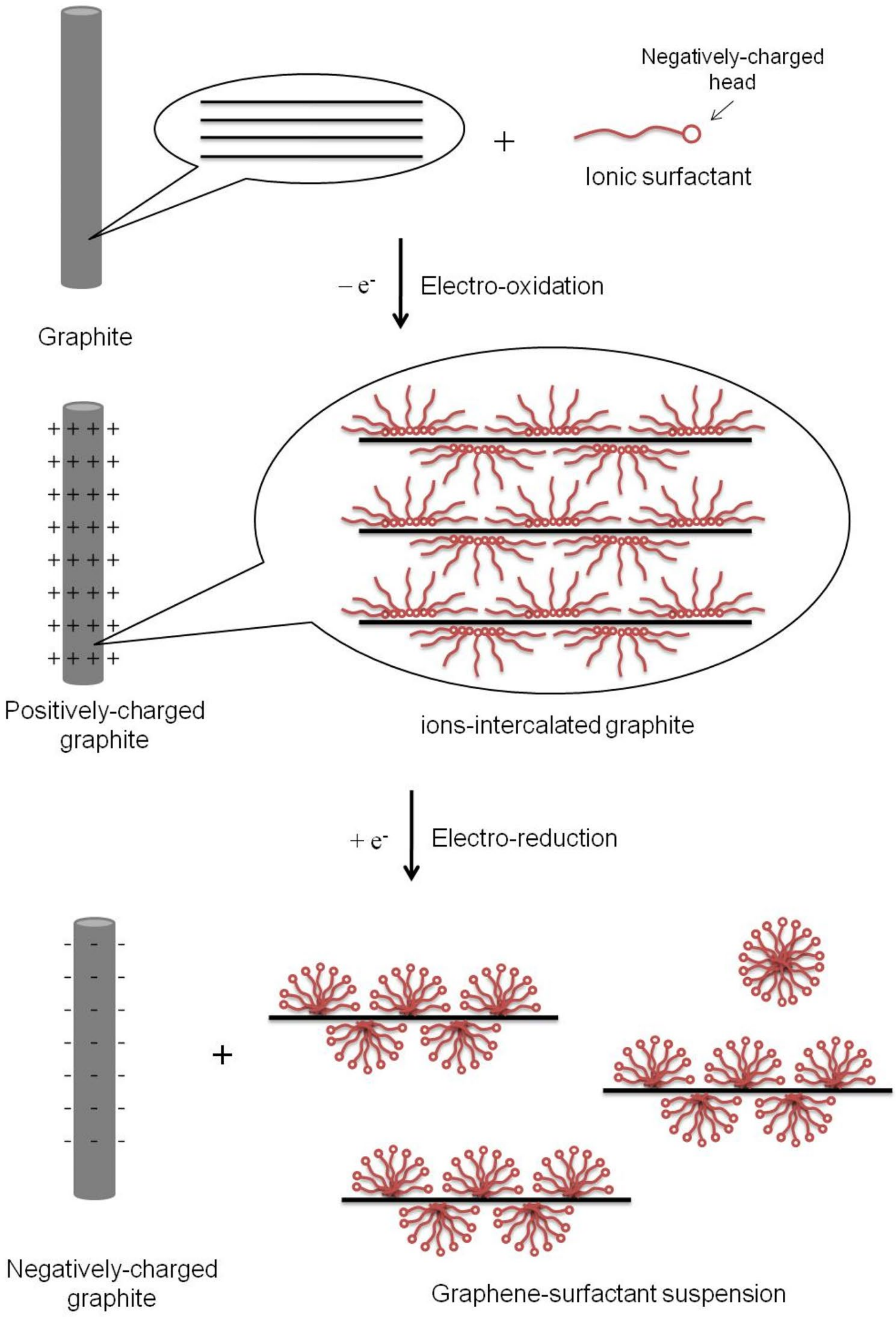
Zhong and Swager [42] reported a two-stage process in the expansion of graphite electrochemically and a direct

**Table 1** A brief summary of electrochemical routes for the production of graphene

| Precursor | Electrolyte | Applied potential (V) | Product | Size (nm) | Thickness (nm) | Layers | Refs. |
|---|---|---|---|---|---|---|---|
| Graphite | $H_2SO_4$<br>$H_3PO_4$<br>$(NH_4)_2SO_4$ | 10 | Graphene | 12.4, 8.7, 8.3, 8.3<br>9.5, 9.1, 8.5, 8.5<br>9.6, 9.2, 8.4, 9.2 | – | Multi | [40] |
| Graphite | SDS | + 2 and − 1 | Graphene flakes | 500 | – | 1 | [41] |
| Graphite foil | $LiClO_4$ in PC → TBA → aryl diazonium salt | − 5 | Functionalized graphene flakes | – | – | < 5 | [42] |
| Waste zinc carbon battery graphite | SDBS | 4.5 | Graphene | – | 2.5 | 2–5 | [43] |
| Paraffin-coated graphite foil | NaOH | 3 | Graphene flakes | – | 0.64 (monolayer)<br>1.27 (bilayer) | < 5 and < 3 | [46] |
| Natural graphite flakes | $H_2SO_4$ | + 10 | Graphene sheets | 10,000 | 0.86 (monolayer)<br>1.5 (bilayer) | 1–4 | [47] |
| Graphite | SDBS<br>NaOH<br>PVP<br>DTAB<br>NaCl | 10 mA (current) | Graphene | – | 0.6<br>9<br>7<br>1.6<br>1.1 | 2<br>30<br>20<br>4<br>3 | [48] |
| Graphite powder | $H_2SO_4$ | + 20 (50 s) and − 20 (20 s) | Graphene | – | 3 | – | [49] |
| Graphite foil | $Na_2S_2O_3/H_2SO_4$ 5:1 | 15 | S-doped graphene nanosheets | – | 0.79 and 0.85 | 1 | [50] |
| Graphite foil | $(NH_4)_2SO_4$ (*aq*) + TEMPO | + 10 | Graphene | – | 2.08 | 2 | [51] |
| Graphite foil | $Na_2SO_4$<br>$(NH_4)_2SO_4$<br>$NH_4NO_3$<br>$(NH_4)_2HPO_4$<br>mixtures of $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ | + 10 | Graphene | 1850<br>1580<br>5210<br>2360 | 1–1.2 | 1, 2, multi | [52] |
| Graphite foil | $(NH_4)_2SO_4 + NH_3 \cdot H_2O$ | 5 | Biomimetic graphene skins | – | – | Multi | [53] |
| Graphite | $Na_2SO_4$ | 2 (5 min) → 10 (5 min) | $MoS_2$/graphene | – | – | Mono and multi | [54] |
| Rolled graphite foils | $Na_2SO_4$ (*aq*) in<br>TEMPO<br>Ascorbic acid<br>$NaBH_4$<br>$C_6H_2(OH)_3COOH$<br>$N_2H_4$<br>HI | 10 | Graphene | 5000–10,000 | 0.74<br>1.32<br>2.01 | 1<br>2<br>3 | [55] |
| Graphite foil | Sodium p-styrenesulphonate (*aq*) | 15 | Polystyrene sulphonate-functionalized graphene nanosheets | > 1 | – | – | [56] |
| Graphite foil | $NaBF_4$ (*aq*) | 10 | Fluorine-modified graphene | 12,000 | 1.6 | ≤ 3 | [57] |

electrochemical functionalization step without the need for any sonication treatment. The graphite rod was initially expanded in a $Li^+$-containing electrolyte and was further expanded in tetra-*n*-butylammonium perchlorate in the second stage [42]. The applied potential of − 5 V was exerted to both stages. The resulting expanded graphite was then subjected to a direct electrochemical functionalization step of aryl diazonium salt, in which less than 5 layers of

**Fig. 1** General mechanism of intercalation and exfoliation for electrochemical synthesis of graphene using ionic surfactant as electrolyte



electrochemically functionalized graphene were obtained. Tiwari et al. [43] reported the facile synthesis of 2–5-layered graphene from electrochemical expansion (ECE) of waste zinc–carbon battery (ZCB) graphite electrodes. A constant concentration of aqueous sodium dodecyl benzene sulphonate (SDBS) was used as electrolyte with an applied voltage of 4.5 V.

Graphene with structural defects is commonly obtained via electrochemical exfoliation technique, which generates oxygen functionalities depending on electrolyte used [44] and exfoliation potential [45]. However, Wang et al. [46] successfully prepared graphene sheets with ~ 100% purity by electrochemically exfoliating the graphite electrode coated paraffin in concentrated sodium hydroxide. In another work, Parvez et al. [47] synthesized high-quality graphene sheets using natural graphite flakes as the working electrode via electrochemical route. The mean thickness for monolayer obtained is 0.86 nm and for bilayer is 1.5 nm. Wang and

Zhang [48] synthesized graphene using the electrical exfoliation method combined with hydroxyl radicals in different types of electrolytes using a current strength of 10 mA. The result demonstrated that the use of SDBS as the electrolyte gives the best exfoliation effect with 89.7% graphene yield using optimal process parameters of 10% (w/v) SDBS solution concentration, 5 g of graphite dosage, and 3 h of exfoliation time. Lim et al. [49] reported that the accumulation of intercalating ions can be avoided by switching the high DC voltage applied successively. This generates graphene with a low introduction of oxygen functional groups, less structural damage with high purity [49].

By means of creating metal-free electrocatalyst with regard to oxygen reduction and oxygen evolution reactions (ORR and OER, respectively), Lee et al. [50] directly synthesized sulphur-doped graphene nanosheets (SDGNs) using thiosulphate as the sulphur source and sulphuric acid as the intercalation compound. The electrochemical exfoliation reaction was supported with ultrasonic treatment for the entire process. The TEM image (Fig. 2a) of the synthesized SDGNs showed minimal appearance of corrugation compared to conventional graphene prepared by Hummers' method. The electrocatalytic performances were systematically explored, and the results revealed that the synthesized SDGNs showed better ORR and OER performances as compared to commercial Pt/C or Ir/C catalyst. Briefly, time-dependent changes in ORR current for the SDGNs electrode exhibited significantly less change (~ 3%) as compared to the Pt/C catalyst which showed 7.3% lower than the initial ORR current (Fig. 2b). These results suggest that the ORR catalytic activity of the SDGNs was better in terms of stability and methanol tolerance. Besides, lower onset potentials and higher currents than the Pt/C (Fig. 2c) indicate the greater OER performance of the SDGNs. The calculated Tafel slopes (Fig. 2d) which correspond to the reaction kinetic at the rate-determining step of the OER indicate that the SDGNs exhibited comparable OER kinetics with Ir/C. On the other hand, Zhao et al. [51] employed the electrochemically exfoliated graphene as an anode material for the ultra-long cycle of lithium ion batteries in which a mixture of ammonium sulphate and TEMPO dispersed in deionized water was used as the electrolyte. The ions present in the solution intercalated in the graphite foil under applied electric field resulted in the expansion of graphite layers and subsequent sonication produced electrochemically exfoliated graphene. The exfoliated graphene was collected using cellulose filters to produce graphene powder which then was dispersed in isopropanol using ultrasonic treatment. The resultant graphene dispersion was directly sprayed

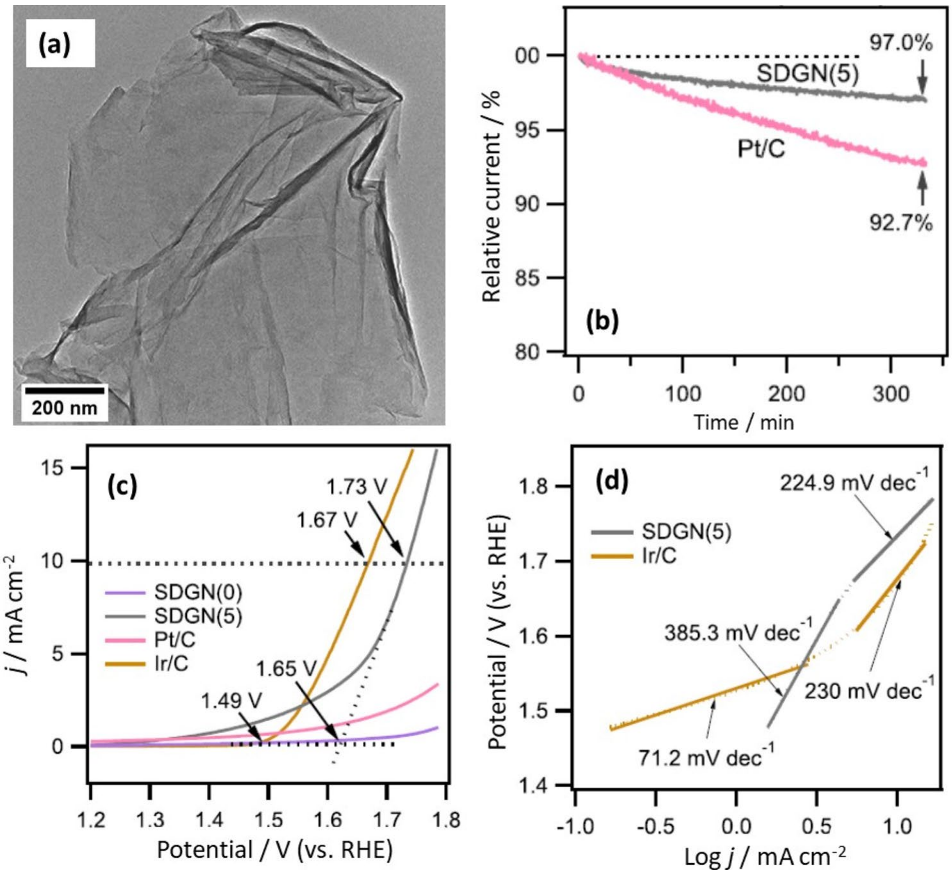


**Fig. 2** **a** TEM image of SDGNs produced by electrochemical exfoliation. **b** Time-dependent changes in ORR current of the SDGNs and Pt/C catalyst. **c** RDE voltammograms for OER of SDGNs, Pt/C and Ir/C. **d** Tafel slopes of SDGNs and Ir/C catalyst [50]

onto the copper foil to be used as the anode material for the lithium ion batteries.

Sharif et al. [52] proposed an approach of producing electrochemically exfoliated graphene with not only greater quality but also with superb high-temperature stability. In their work, inorganic electrolytes (e.g. diammonium phosphate and ammonium sulphate and different combinations of these salts) were used, and it was found to produce graphene with larger lateral size and a lower amount of oxygen functional groups compared to other types of electrolytes. The synthesized graphene can withstand temperature up to 750 °C in the air, which is uncommon in the carbon families of high surface area as they are unstable around 400–500 °C in air. Tang et al. [53] successfully fabricated biomimetic graphene skins on the surface of stainless-steel mesh with superhydrophobic and superoleophilic characteristics, which enables the separation of oil and water mixture. The hydrophobicity of the graphene was increased when the graphene structure was formed into dendritic structure attained by introducing a small amount of metal ions during the electrochemical reaction. The introduction of metal ions changed the shape of the graphene on the surface of the skin into dendritic shape. The experiment was carried out using mixtures of ammonium sulphate and ammonia water at a voltage of 5 V. The schematic diagram of peeling mechanism of the graphene is presented in Fig. 3.

Ali et al. [54] reported an electrochemical synthesis of $MoS_2$/graphene composite by combining both $MoS_2$ crystal and graphite rod as the anode while a platinum wire was set as the cathode. In an electrolyte of 1 M sodium sulphate, a voltage of 2 V was employed for 5 min followed by a voltage of 10 V for 5 min. The composite exhibited a high specific capacitance of 227 F $g^{-1}$, which showed great electrochemical stability and low electrical resistance. Yang et al. [55] reported that the addition of antioxidants (TEMPO, ascorbic acid, and sodium borohydride) into the aqueous ammonium sulphate electrolyte eliminates both hydroxyl and oxygen radicals, thus reducing the formation of defects on graphene. Graphene that was prepared by using TEMPO showed the lowest amount of oxygen (3.8%) compared to the other two, and the value is just slightly above the pure graphite (1.7%). The graphene ink was then applied in the application of transparent conductive films and flexible supercapacitors using dimethylformamide.

Zhao et al. [56] showed a promising method to produce polystyrene sulphonate (PSS)-functionalized graphene nanosheets in which the bulk graphite was electrochemically exfoliated for 6 h followed by a simple free radical polymerization (in solutions containing ammonium persulphate and ammonium sulphite) to initiate p-styrene sulphonate polymerization. The electrochemical exfoliation process of the functionalized graphene is presented in Fig. 4. The work not only emphasized on the potential of *p*-styrene sulphonate for exfoliation and functionalization of graphene but also pointed out its good compatibility on the surface of graphene. Besides, high quality of non-covalently functionalized graphene nanosheets with few defects was produced. The study also revealed that the functionalized graphene nanosheets incorporated in polystyrene nanocomposites showed improved thermal and mechanical properties as compared to pure polystyrene. Zhou et al. [57] developed a scalable production of high-quality solution-processable fluorine-modified graphene nanosheets via a one-step electrochemical exfoliation method for flexible and high volumetric energy density on-chip ionogel-based micro-supercapacitors. Typically, graphite foil was electrochemically exfoliated in an aqueous fluorine-containing neutral electrolyte for 15 min with an applied voltage of 10 V.

The electrochemical exfoliation of graphene can be summarized as follows:

1. *Types of electrolyte* The selection of electrolyte or surfactant will in turn determine the mechanism involve in the exfoliation of graphene and the quality of the product. Different electrolyte used may yield different types of graphene products.
2. *Concentration of electrolyte* The environment of the intercalation mechanism might be affected by the concentration of the ions or electrolyte. Higher concentration of electrolyte provides higher ions intercalation in the electrode active sites. Besides, the usage of a surfactant as the electrolyte require certain critical concentration for micelles formation.
3. *Types of electrode* The electrochemical exfoliation of graphene usually involved the usage of graphite as the electrode precursor such as graphite foil, paraffin coated graphite foil, graphite flakes, graphite powder, and waste zinc carbon battery graphite.
4. *Applied potential* Various applied potentials can be used which influenced the exfoliation yield of the graphene. The selection of suitable potential may be dependent on the electrolyte or ionic liquids used.

## 2.2 Electrochemical exfoliation of GQDs

In this section, several works on the synthesis of graphene quantum dots (GQDs) using electrochemical exfoliation method are summarized in Table 2. Graphite, carbon fibres, graphene oxide, and multi-walled carbon nanotubes have been used as precursors in the synthesis of GQDs with different sizes and layers. For example, Tan et al. [58] synthesized 3-nm uniform-sized GQDs via electrolysis of graphite rod in an aqueous solution of 0.01 M potassium persulphate at potential of + 5.0 V. They observed that the potassium persulphate plays a vital role as the supporting electrolyte to generate a red fluorescent GQDs under 365-nm irradiation.

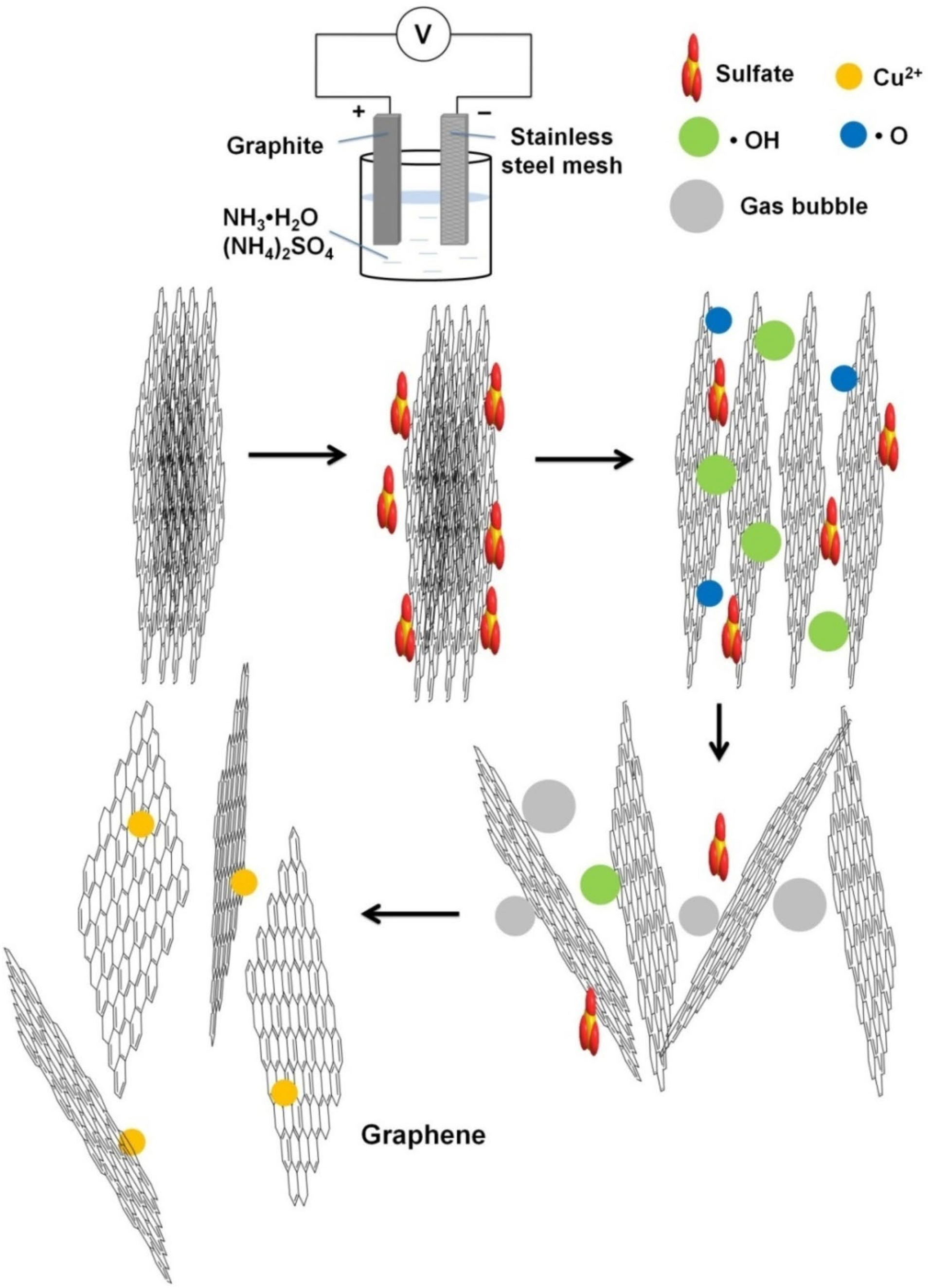


**Fig. 3** Schematic diagram of mechanism for the exfoliation of graphene according to Tang et al. [53]

When sodium sulphate was used as the supporting electrolyte, a very weak red photoluminescence was observed, whereas no fluorescent was observed when potassium persulphate was replaced with potassium ferrite. This indicates that the selection of the sulphate electrolyte is crucial for the generation of the red fluorescent GQDs. Large anodic voltage discharging of the sulphate ions, $SO_4^{2-}$ resulted in the production of peroxydisulphate ions, $S_2O_8^{2-}$. The presence of sulphate radicals generated by electrochemical reaction of the $S_2O_8^2$ ions serves as electrochemical “scissors” and is the key factor to produce the GQDs.

Huang et al. [59] synthesized amino-functionalized GQDs in a weak electrolyte, ammonia solution using an electrochemical oxidation and cutting reactions. During the synthesis, GQDs were rapidly produced, with a product yield of 28% (after 120 min) and the amino-functionalization can be influenced by manipulating the electrolyte concentration. They revealed that the usage of the weak electrolyte produced higher yield, better crystallinity, and lower defects of GQDs as compared to the GQDs produced using strong electrolyte. Briefly, mechanism of electrochemical exfoliation occurring in strong electrolyte caused the graphene

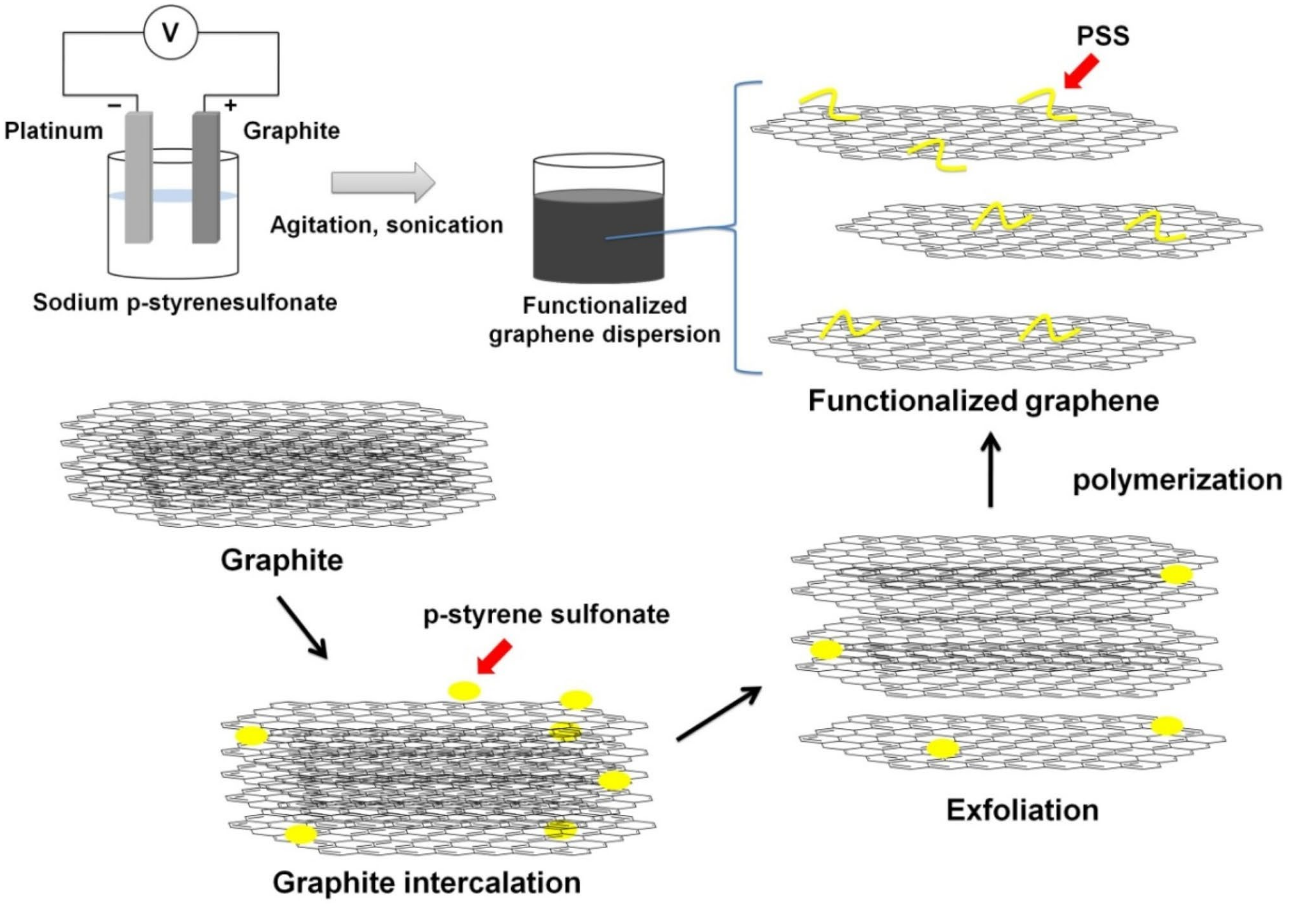


**Fig. 4** Schematic diagram of electrochemical exfoliation of PSS-functionalized graphene [56]

sheets to be promptly broke and exfoliated apart due to the harsh environment created by the strong electrolyte system, thus forming low yield of GQDs. However, in a weak electrolyte system, the GQDs were continuously and efficiently formed due to the lengthened and effective oxidation interaction (enhanced cutting effect) and suppressed intercalation-induced exfoliation. On the other hand, Yan et al. [60] aimed to synthesize functionalized GQDs at large scale using carbon fibre as anode and platinum wire as the counter electrode in a mixture of ionic liquid with different ratios of water under an applied potential of 6 V. The schematic illustration of electrochemical exfoliation of GQDs using carbon fibre electrode is presented in Fig. 5. The ratio of water at 0, 15, and 30% in the electrolyte generated blue-emitting GQDs, green-emitting GQDs, and yellow-emitting GQDs, respectively, under 365-nm irradiation. Such phenomenon of various colour emissions is reasonably influenced by the size of the GQDs obtained whereby the average lateral size of the blue-, yellow-, and green-emitting GQDs was found to be around ~2, 3, and 4 nm, respectively. This revealed that the quantum confinement or size-dependent effect can be accentuated by varying water content in the ionic liquid used whereby 0% water content contributes to smaller size GQDs, while water-rich electrolyte produced slightly larger size of GQDs. Other factors include surface functionalization and defects of the GQDs, and liquid structure of the ionic liquids which can also be affected when water was added in the electrolyte [60].

In another work by Deng et al. [32], graphite oxide (GO) can be etched into GQDs. In the synthesis process, two Pt sheets were set as both anode and cathode, the GO powder was used as reactant, and interestingly, pure water was solely used as the electrolyte. The synthesis involved an applied voltage of 15 V which is high enough for water to be oxidized, thus generating an ample amount of hydroxyl and oxygen radicals at the anode [32]. These radicals can be absorbed onto the GO, thus making a delicate structure of GO during stirring, which consequently produces the GQDs. Zhang et al. [61] managed to electrochemically synthesize GQDs using the graphite rod as anode and Pt foil as cathode in an alkaline aqueous solution of NaOH. The product of electrolysis was then treated with hydrazine hydrate at room temperature to induce the reduction of graphene oxides to yellow luminescent GQDs. As shown in

**Table 2** A brief summary of electrochemical routes for the production of GQDs

| Precursor | Electrolyte | Applied potential (V) | Product | Size (nm) | Layers | Refs. |
|---|---|---|---|---|---|---|
| Graphite | $K_2S_2O_8$ | + 5 | GQDs | 3 | – | [58] |
| Graphene paper | $NH_3$ | 30 | GQDs | 3–8 | 1–4 | [59] |
| Carbon fibre | ([BMim][$BF_4$]) + $H_2O$ 0%<br>$H_2O$ 15%<br>$H_2O$ 30% | 6 | Blue GQDs<br>Green GQDs<br>Yellow GQDs | 2.4 ± 0.6<br>3.1 ± 0.5<br>4.2 ± 0.5 | Fewer layers | [60] |
| Graphene oxide powder | $H_2O$ | 15 | Purple blue GQDs<br>Blue GQDs<br>Green GQDs | 2.4 ± 0.3<br>3.6 ± 0.2<br>4.6 ± 0.4 | 1 or few layers | [32] |
| Graphite | NaOH | – | GQDs | 5–10 | 1 | [61] |
| Graphite | Milli-Q water + 1 M citric acid monohydrate + NaOH<br>1.5 M<br>2 M<br>3 M<br>4 M | + 10 | GOQDs<br>GOQDs<br>GQDs<br>GOQDs | 2.24–3.04 | – | [31] |
| Multi-walled carbon nanotubes | Propylene carbonate + $LiClO_4$ | − 1 to + 1.1 | Green GQDs | 3.2 (15 h)<br>5 (11 h)<br>8.2 (7 h) | 1–3 | [62] |
| 3D graphene | 1-butyl-3-methylimidazolium hexafluorophosphate in acetonitrile | 5 | Blue GQDs | 3 | 1 | [33] |
| Graphite | $CH_3ONa$ in $H_2O$<br>$CH_3ONa$ in $CH_3OH$ | 100 mA/cm$^2$ (current density) | Yellow GQDs<br>Green GQDs<br>Blue GQDs | 3.5 ± 0.5<br>5.8 ± 0.7<br>7.3 ± 0.4 | – | [63] |
| Graphite | $C_6H_6Na_{12}O_{24}P_6$ | 5 | Yellow GQDs | 2–4 | – | [25] |
| Graphene oxide | $LiClO_4$ + propylene carbonate | + 1.05 (16 h) and − 1.05 (3 h) | GQDs | 3–5 | – | [64] |
| Graphite | $C_6H_6Na_{12}O_{24}P_6$ + $Na_2S$ + NaOH<br>$Na_2S$ + NaOH<br>$C_6H_6Na_{12}O_{24}P_6$ | 5 | P, S-GQDs<br>S-GQDs<br>P-GQDs | 3.2 | – | [34] |
| Graphene film | Phosphate buffer solution | – | Blue GQDs | 52 ± 13 | 1–3 | [65] |
| Graphite | NaOH + semicarbazide + $H_2O$ | 5 | Blue GQDs<br>Red GQDs<br>Green GQDs | 20 | – | [66] |
| Coke | MeOH + $H_2O$ + $(NH_4)_2S_2O_8$ | 80–400 mA/cm$^2$ (current density) | Orange GQDs<br>Yellow GQDs<br>Green GQDs<br>Blue GQDs | 4.61 ± 0.88<br>4.15 ± 0.54<br>3.02 ± 0.45<br>2.90 ± 0.46 | 3–4<br>3–4<br>2–3<br>2–3 | [35] |

the reaction mechanism (Fig. 6), during the electrochemical anodic oxidation, hydroxyl and oxygen radicals produced act as "scissors" to form oxygenated graphene sheets. The next step involved the reduction process using hydrazine to produce a homogeneous GQDs colloidal solution although large and agglomerated graphene sheets also have been formed.

In the reported work of Ahirwar et al. [31], GQDs/GOQDs were electrochemically produced by a combination of citric acid monohydrate and alkali hydroxide in Milli-Q water as the electrolyte. The mechanism of electrochemical production of the GQDs is illustrated in Fig. 7. Prior to the experiment, the graphite rod was heated at high temperature to generate surface defects in order to facilitate the electrochemical exfoliation process. Shinde and Pillai [62] synthesized 3, 5, and 8 (± 0.3) nm GQDs at 90 °C using a two-step process utilizing multi-walled carbon nanotubes (MWCNTs) as the precursor, whereas propylene carbonate and lithium perchlorate were used as the supporting electrolyte. The method offers the production of size-tunable GQDs whereby 23 (± 2) nm GQDs were obtained at 30 °C temperature using identical electrochemical approach. A facile procedure to synthesize high-quality GQDs from three-dimensional (3D) graphene was reported by Ananthanarayanan et al. [33] using an applied voltage of 5 V for 100 s to generate GQDs with an average size of 3 nm and a thickness of 1.25 nm equivalent to a single layer.

Muthurasu et al. [63] utilized a simple two-step reaction in the synthesis of GQDs and reduced graphene oxide (RGO) simultaneously. Graphite rod and platinum foil were, respectively, set as anode and cathode. Both electrodes were

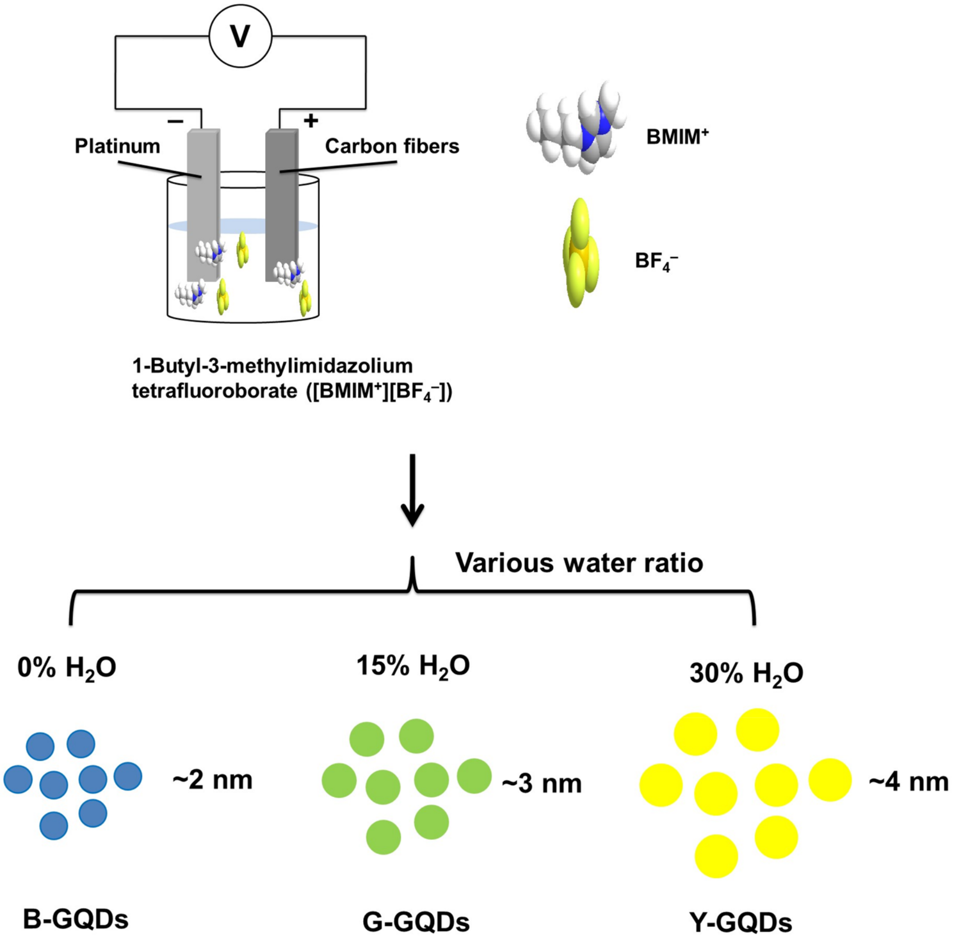


**Fig. 5** Schematic illustration of the production of multi-colour emission of GQDs using ionic liquids-assisted electrochemical exfoliation of carbon fibre electrode [60]

immersed in an electrolyte of 0.1 M sodium methoxide in water with an applied constant current for 3 h. Glucose (0.1 M) and 1 ml of hydrazine monohydrate were used as reducing agent in a different portion of the solution. The emission colour of the GQDs can be tuned between yellow and green by varying the nature of the reducing agent in the aqueous medium. In another work, Li et al. [25] successfully synthesized phosphorus-doped GQDs (P-GQDs) with a high content of phosphorus by using a green food antioxidant additive, sodium phytate ($C_6H_6Na_{12}O_{24}P_6$) as the electrolyte. The working electrode, graphite was electrochemically exfoliated at 5 V for 12 h. The obtained P-GQDs showed good monodispersed and spherically shaped under the TEM image.

Using GO as the precursor, Kalita et al. [64] directly synthesized GQDs through an electrochemical approach with propylene carbonate and lithium perchlorate as electrolytes. The synthesis involves oxidation reaction followed by a reduction reaction, and the GQDs synthesized were then applied as soil moisture sensors. Peng et al. [34] synthesized GQDs co-doped with phosphorus and sulphur via one-step electrolysis in an alkaline solution containing sodium phytate and sodium sulphide. Sodium hydroxide was added into the electrolyte to increase the production of oxygen and hydroxyl radicals to facilitate P and S doping into the GQDs' graphitic structure to increase the electrochemiluminescence (ECL) performance.

Luo et al. [65] synthesized GQDs from graphene film through electrooxidation method with 3–5 nm of average size. After the electrooxidation process, the obtained electrolyte aqueous solution containing the GQDs was dialyzed with a dialysis bag with different pore sizes. The usage of dialysis bag with 8000–14,000 molar mass cut-off successfully obtained a large size GQDs with an average diameter of 52 nm and emitted blue emission under 365-nm irradiation. The smaller size of the GQDs (several nanometers) can be obtained using a dialysis bag with 1000 molar mass cut-off. Fu et al. [66] reported the first electrochemical synthesis of N-doped GQDs to use semicarbazide. The average diameter of GQDs obtained is 20 nm, and they have the capability to emit 3 basic colour fluorescence (green, blue, and red) independently due to edge and quantum confinement effects.

In another work, He et al. [35] electrochemically synthesized multi-coloured fluorescence GQDs (orange, yellow, and green) from a small cuboid coke lump by regulating the current density and adjusting the water content of

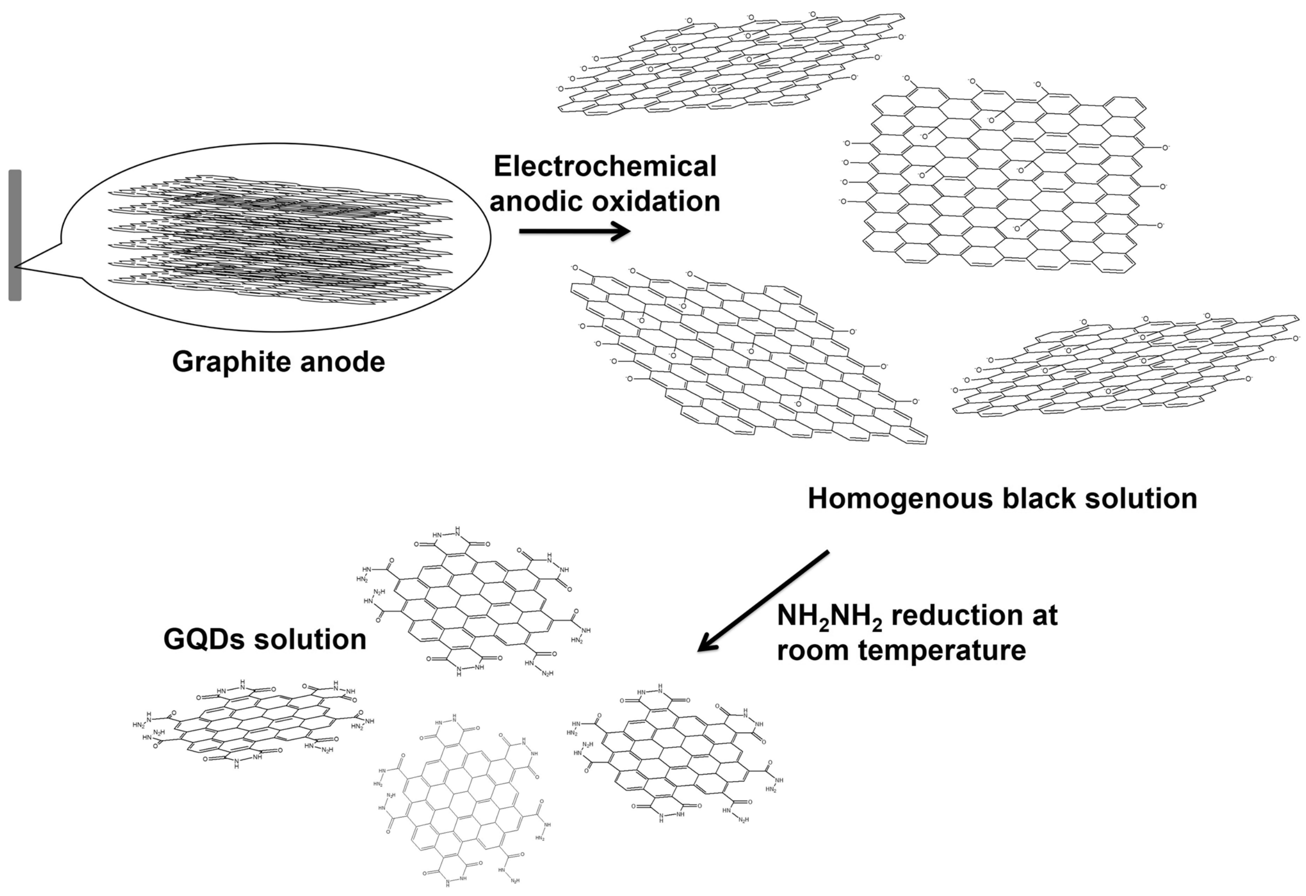
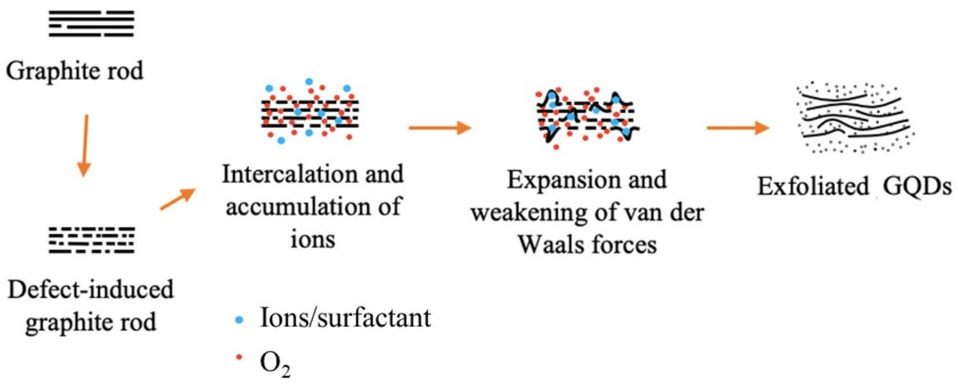


**Fig. 6** Schematic illustration of GQDs production via electrochemical oxidative cleave using radicals and hydrazine reduction at room temperature [61]

**Fig. 7** Mechanism involved for the electrochemical preparation of GQDs adapted from Ahirwar et al. [31]



electrolyte solution. The electrolyte used contains a mixture of water and methanol in the range between 10:90 and 85:15 with 0.1 M ammonium persulphate at pH 7, and the current density applied was from 80 to 400 mA/cm$^2$. Bright blue GQDs were synthesized from the green GQDs through chemical reduction using $NaBH_4$. The schematic diagram of mechanism of the exfoliation is shown in Fig. 8. Briefly, the exfoliation employed the electrochemical "scissors" process of the coke using oxygen and hydroxyl radicals. These active radicals fiercely attack the coke edge planes, and subsequent intercalation of sulphate radical and exfoliation of the split graphene sheets resulted in the formation of nano-sized GQDs. The current density and water content play a critical role in the production of GQDs with multi-coloured emission. The higher current density imparts more powerful exfoliation of the coke particles into smaller size GQDs [35]. As mentioned earlier, the different colour emission can be caused by the quantum confinement or size-dependent effect.

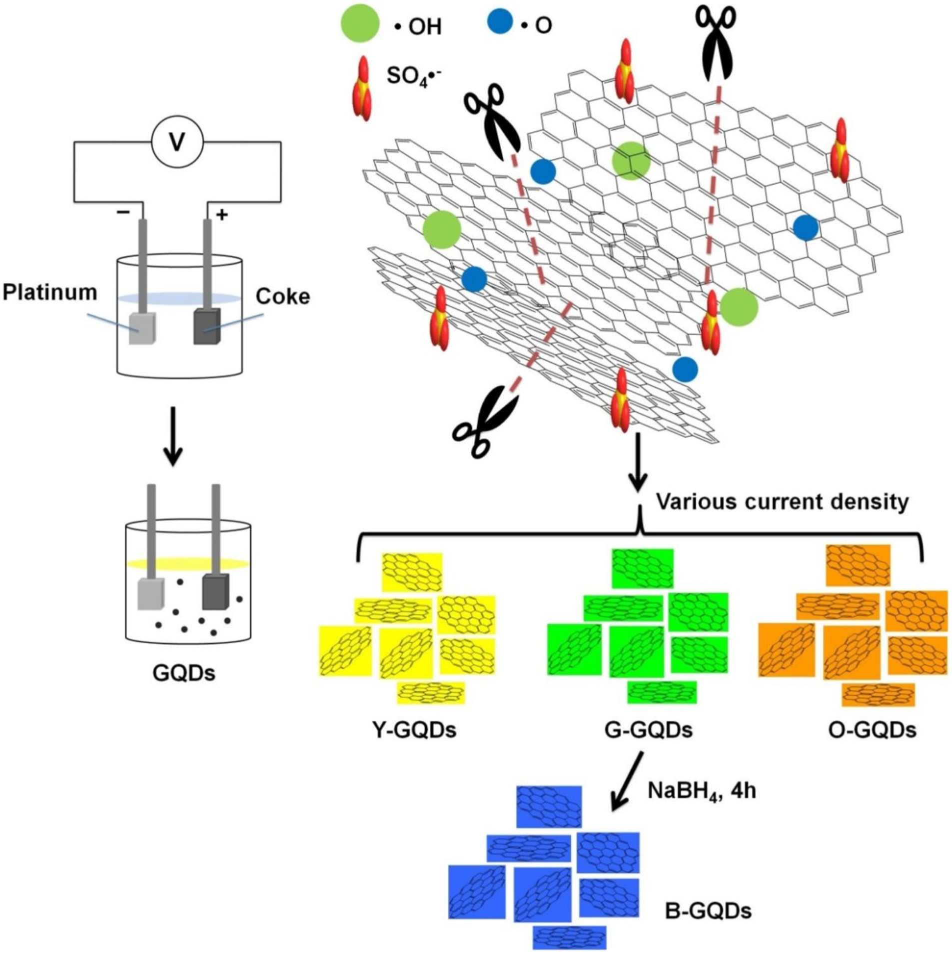


**Fig. 8** Schematic illustration of electrochemical "scissors" process of coke edge planes by radicals which resulted in the formation of GQDs products [35]

Thus, higher current density produced shorter-wavelength emission, while lower current density results in the production of GQDs longer-wavelength emission. Besides that, the surface modification may also affect the colour emission wavelength. For instance, the green GQDs were subjected to reduction using $NaBH_4$, thus producing blue-fluorescent GQDs. This can be explained by the transformation of C=O groups into –OH groups which resulted in the decrease of surface defects, while the integrity of the π-conjugated system was increased [35, 67]. This surface transformation consequently produced blue-emission GQDs.

The electrochemical exfoliation of GQDs can be summarized as follows but not limited to:

1. *Electrode precursor* Range of electrode precursor can be used for the electrochemical production of GQDs such as graphite, carbon fibres, graphene oxide, and CNTs. The surface modification of the electrode such as surface defects induced by heating process also allows the formation of GQDs via the electrochemical reaction.
2. *Types of electrolyte* Similar to electrochemical exfoliation of graphene, the mechanism of GQDs production is very much dependent on electrolyte or supporting electrolyte used. The presence of electrochemical "scissor" of the ions plays a significant role on the exfoliation of GQDs. The yield, crystallinity, and defect density of the GQDs also related to the types of electrolyte used.
3. *Various water contents* Different ratio of water content of the electrolyte used may influence the size and colour emission of the GQDs due to quantum confinement effect.
4. *Current density* Another crucial factor that affects the product of GQDs is the current density used during the electrochemical process. High current density allows more exfoliation strength which produces smaller size of GQDs.

## 3 Advantages and challenges of electrochemical technique

This technique carries many advantages for the production of graphene and GQDs. When compared to other techniques, electrochemical exfoliation offers the production of high-grade graphene sheets at a larger scale [68]. A basic electrochemical cell usually involves two electrodes immersed in an electrolyte with a direct current source. The degree of oxidation, defect density, size, thickness, and number of layers of synthesized graphene are fundamentally controlled by the processing parameters which include current or voltage applied, reaction time, type and concentration of electrolyte [69, 70]. Special equipment is not needed for this method and the condition is usually done at room temperature [40]. Instead of using strong oxidants like in the Hummers method, the electrochemical method makes use of the graphite's electrical conductivity to intercalate charged ions and the subsequent exfoliation process further takes place during the electrochemical reaction of these ions [2].

Besides having the capability to create functionalized graphene, electrochemical routes promise excellent suspension stability of graphene in surfactants. The colloidal graphene/SDS suspension synthesized by Alanyalioğlu et al. [41] via this method utilizing SDS-intercalated graphite electrode was reported to be stable for over 8 months. In addition, the electrochemical method can efficiently prevent issues pertaining to poor crystallization of carbon nanostructures products when GQDs were synthesized using cyclic molecules in the bottom-up routes [59, 71, 72]. The electrochemical method under top-down routes is regarded as the best method to prepare GQDs towards green and bulk-scale [59]. The method is simple in which extreme reaction conditions can be avoided, thus making the procedure rather efficient and feasible as compared to other conventional top-down or bottom-up approaches [59, 62]. Furthermore, the electrochemical method provides benefits in terms of cost-saving, scalable, economical, and simple operation [32].

However, the usage of electrochemical exfoliation method to obtain high-quality graphene with homogeneous size and well-distributed layers remains a challenge. The synthesis of monolayered and multi-layered graphene sheets with different sizes has been reported in several works. Besides, the intercalation of ions at anodic potential will most likely cause the graphite to be oxidized, thus disrupting the $sp^2$-hybridized carbon network. Unfortunately, no electrochemical or chemical processes are capable of reversing the process of forming pure graphene back. Other than that, the electrochemical properties of graphene will greatly be affected due to the existence of both oxygen functional groups and structural damage. The usage of surfactants as electrolyte may contribute to the generation of functionalized graphene which, in return, also affects the electrochemical properties [8, 73–75]. Another matter regarding the challenges of the electrochemical method is the efficiency to synthesis GQDs at high yield. Two general processes occur during anodic exfoliation, namely, intercalation–exfoliation and oxidation-cutting effects. The intercalation–exfoliation process will rapidly cause graphene flakes or sheets to detached from the anode, and these exfoliated portions are not being oxidized or further cut, thus synthesizing GQDs in a very small output ($< 1\%$) [59].

In an electrochemical cell, graphite electrodes can be exfoliated, intercalated with heterogeneous molecules, and dispersed in solutions by applying the driving potential in either aqueous or non-aqueous electrolytes. Generally, the routes of electrochemical exfoliation can be divided into cathodic and anodic exfoliation. Cathodic exfoliation occurs when voltage is applied to graphite that is attached to the cathode, and the graphene sheets are exfoliated by the intercalating cations [49]. The intercalation of cations (mostly in organic electrolytes) is not conditioned to be oxidized, therefore preventing the finished products from being adorned with groups containing oxygen. However, a few layers of graphene are frequently produced and require prolonged sonication or other several conditions such as microwave irradiation to isolate them [42, 55, 76, 77].

During anodic exfoliation, the graphite anode is intercalated with anions [49]. The intercalation of anions (mainly in aqueous electrolytes) requires a short time and can be done less than an hour. As summarized in Table 1 and Table 2, aqueous solutions of mineral acids and mineral salts are usually used as electrolytes with graphite functioning as the anode. Unfortunately, the positive voltage applied, especially in acidic electrolytes, usually produces graphene containing oxygen functional groups [55, 78, 79]. In addition, the application of high anodic potential results in both oxidation and structural damage although relevantly, it is not as extensive as the chemically produced graphene oxide [7, 80]. Due to the application of constant voltage, both routes face issues throughout the electrochemical exfoliation process where the intercalating ions accumulated at the interlayers of graphite, thus causing a reduction of output and degradation of the produced graphene sheets' quality [49].

Briefly, the intercalation of anions through anodic potential allows significant introduction of oxygen functionalities on the exfoliated graphene product. This consequently produces more defective graphene materials and affects the electrical properties of the graphene. However, the anodic potential allows far more efficient exfoliation of graphene as compared to cathodic potential mechanism. This is due to concomitant formation of radical species which facilitates more available opening for anions penetration and intercalation. Albeit lower-quality graphene with more surface defects is produced, the anodic potential process offers efficient and significantly accelerated exfoliation process. In contrast, the cathodic exfoliation process through the intercalation of positive ions offers better quality of graphene product at the cost of slower and less efficient process as compared to anodic exfoliation [81]. Therefore, the anodic exfoliation may be the preferred method although the defects presence affects the mechanical properties and applicability of the graphene for electronic applications. However, it should be note that the presence of the edge and plane defects could be also beneficial, particularly for electrochemical applications.

## 4 Applications of electrochemically prepared graphene and GQDs

The remarkable properties of graphene and GQDs have not only triggered researchers to explore fundamentally but also have unlocked their potential to be incredibly useful in various fields of applications. Both graphene and GQDs are undoubtedly useful for nanocomposites application with a wide range of targeted matrix or marriage candidates [2, 19]. The scope of nanocomposites application is tremendously huge, in which the types of nanocomposite designed in turn determine the specific targeted application. For examples, Sayah et al. [82] reported the incorporation of electrochemically synthesized graphene into polyaniline matrix and fluorine-doped tin oxide (FTO) composite for the preparation of supercapacitor electrode material. Achee et al. [83] demonstrated that the electrochemically exfoliated graphene can be used as conductive filler for polycarbonate composite via solution casting. Besides, the electrochemical technique often produces stable and dispersible graphene or GQDs products, which significantly allow direct assembly and facile composite processing. For instance, by taking the advantages of stable water-dispersible graphene produced by electrochemical exfoliation, Qiu et al. [84] prepared graphene–polyvinyl alcohol (PVA) composite films and reported the remarkable increased of tensile strength and improved of flame-retardant properties of the PVA composites.

On the other hand, Li et al. [85] reported that their nitrogen-doped GQDs (N-GQDs) prepared via the electrochemical method using tetrabutylammonium perchlorate (TBAP) in acetonitrile as the electrolyte exhibited electrocatalytic property which is comparable to the conventional Pt/C catalyst for the oxygen reduction reaction. Apart from the superior electrocatalytic activity, the N-GQDs produced showed unique optoelectronic and luminescence properties which can be viable for bioimaging and light-emitting diodes application [85]. Similarly, Lee et al. [50] reported the significant electrocatalytic application of the electrochemically exfoliated SDGNs, whereby the ORR catalytic activity of the SDGNs was better in terms of stability and methanol tolerance to commercial Pt/C. Ananthanarayanan et al. [33] have synthesized GQDs from 3D graphene for optical detection of $Fe^{3+}$ ions, while Muthurasu et al. [63] utilized the electrochemically produced GQDs for bioimaging and cytotoxicity studies. Briefly, the ionic liquid used in the electrochemical strategy by Ananthanarayanan et al. [33] not only accommodate the stable dispersion and exfoliation of GQDs but bestow the GQDs with the ability for sensitive and specific optical detection of $Fe^{3+}$ ions. It is undoubtedly recognized that the GQDs exhibited photoluminescence properties which endows GQDs for bioimaging application as reported by Muthurasu et al. [63]. Besides that, Parvez et al. [47] introduced the exfoliated graphene as conductive electrodes to be applied in organic electronic devices, while Wang et al. [46] electrochemically prepared graphene sheets to be used in transparent conductive films. The outstanding transparency and good conductivity of the electrochemically exfoliated graphene produced by Wang et al. [46], and Parvez et al. [47] thusly show promising potential to replace the expensive indium tin oxide as the transparent conductive film as well as hold promise for organic electronic devices application. The electrochemical synthesis of graphene towards the application of the supercapacitor electrode was also reported by Tiwari and co-workers [43], whereby the remarkable value of specific capacitance was obtained as compared to other similar reported works. The applications of electrochemically exfoliated graphene and GQDs are summarized in Fig. 9.

## 5 Conclusion

In conclusion, various routes and mechanisms of electrochemical exfoliation of graphene and GQDs as discussed above can be rapid, feasible, efficient, reliable, and cost-effective. Besides, most of the electrochemical methods

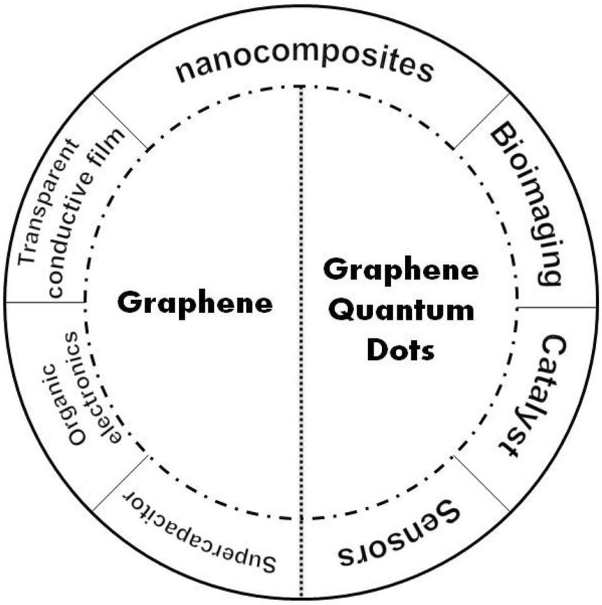


**Fig. 9** The applications of electrochemically exfoliated graphene and GQDs

highlighted seem applicable to be scaled up for large production of graphene and GQDs depending on the size of the electrochemical set-up. This review has not only summarized several works on the preparation of graphene and GQDs via electrochemical method but also provided an insight into the advantages and challenges faced by the top-down electrochemical preparation routes, which will open doors for more innovative and sensible way in fabricating graphene or GQDs from a wide range of precursors, chemicals and parameters. On the other hand, we believe that this review might pave the way towards the development of scalable production of graphene and GQDs and will unlock windows of opportunities for multitude range of applications.

**Acknowledgements** This work was supported by the Fundamental Research Grant Scheme (FRGS/1/2018/STG01/UIAM/03/2) (FRGS19-015-0623), Ministry of Higher Education (MOHE), Malaysia and Department of Chemistry, Kulliyyah of Science, International Islamic University Malaysia.

## Compliance with ethical standards

**Conflict of interest** On behalf of all authors, the corresponding author states that there is no conflict of interest.

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