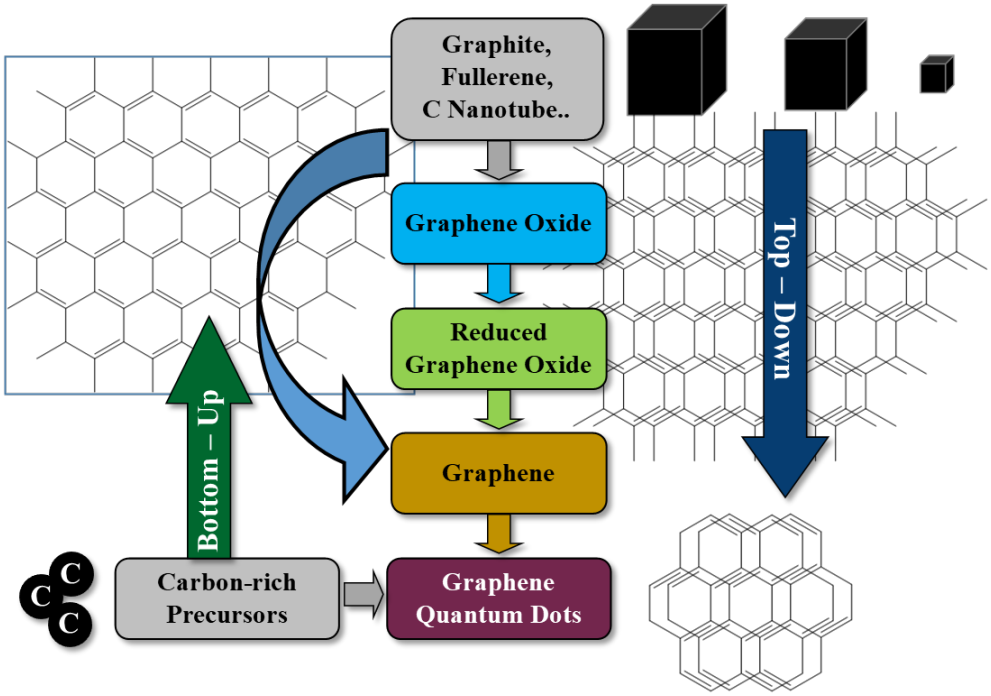
REVIEW ARTICLE

Graphene quantum dot (GQD) synthesis: A review of the methods, challenges and future prospects

K. Wijayaratne, T.M.A.A.B. Thennakoon and T.M.W.J. Bandara*



Highlights

- GQD, the newest member of the carbonaceous materials, is under the research spotlight.
- GQDs can significantly improve the performance of numerous applications.
- A multitude of methods are used to synthesize, characterize, and optimize GQDs.
- New approaches should be innovated, and existing should be optimized for GQD synthesis.
- Synthesis techniques, challenges, and future directions of GQD research are reviewed.

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REVIEW ARTICLE

Graphene quantum dot (GQD) synthesis: A review of the methods, challenges and future prospects

K. Wijayaratne[1], T.M.A.A.B. Thennakoon[1,2], and T.M.W.J. Bandara[1*]

[1]Department of Physics and Post Graduate Institute of Science, Faculty of Science, University of Peradeniya, Peradeniya, 20400, Sri Lanka.
[2]Department of Physics, University of Virginia, Charlottesville, VA 22904, USA.

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Abstract: Unique properties of dimensionally confined nanoparticles are successfully utilized in improving the performance of numerous applications. The quantum confinement effect and related opening of bandgap can be used to engineer optoelectrical properties, thus broadening their applicability in various fields. From a materials standpoint, carbonaceous materials such as graphene have recently attracted much attention among researchers. Graphene quantum dots (GQDs), the newest member of the carbonaceous material family, is of particular interest due to their distinct electronic, optical, chemical, and mechanical properties. GQDs can be customized and optimized by varying the size and number of graphene layers, doping, attaching functional groups and heteroatoms, or making composites. Apart from band structure, GQDs possess many other favorable functional properties required for various applications. Some desirable features include tunable fluorescence, high quantum efficiency/ quantum confinement, higher chemical stability, edge effects, biocompatibility, low toxicity, photostability and water solubility. In this mini review, reliable GQD fabrication techniques are discussed, emphasizing the requirements, strengths, weaknesses and specialties of each technique. Further, challenges and future prospects of GQDs are also discussed.

***Keywords*:** quantum dot; graphene quantum dot; GQD; quantum confinement; bottom-up synthesis; top-down synthesis.

INTRODUCTION

Graphene is a 2-D carbon structure in which carbon atoms are arranged in hexagonal rings ith sp^2 carbon-carbon bonds (bond length: 0.142 nm). A sheet of graphene can extend infinitely in two dimensions (Sharma, 2020; Bandara *et al*., 2022b). Such 2-D structures rolled into carbon nanotubes (CNTs) are considered 1-D structures. In addition, graphene can be wrapped into Buckyballs forming fullerenes which are regarded as 0-D structures. The evolution of functional carbonaceous material is summarized in Figure 1. Graphene quantum dots (GQDs) are the newest member of the family. GQDs are nanoparticles comprised of single to few graphene layers and exhibit quantum confinement. Despite graphene being a zero bandgap material, GQDs can be fabricated to have a non-zero bandgap (Lomeda *et al*., 2008; Zacharias *et al*., 2021; Bandara *et al*., 2022a). GQDs have attracted the attention of researchers due to their distinct electronic, optical, chemical, and mechanical properties. GQDs can be customized and optimized by varying the size and number of graphene layers, doping, attaching functional groups and heteroatoms, or making composites (Zhao *et al*., 2015; Wang *et al*., 2016b; Zhang *et al*., 2018; Wang *et al*., 2019). In addition, GQDs possess many favorable functional properties suitable for a range of applications. For example, tunable fluorescence, high quantum efficiency/quantum confinement, higher chemical stability, edge effects, biocompatibility, low toxicity, photostability, and water solubility enhances the range of practical applicability. GQDs can be used in a variety of applications such as biological imaging, biomedical devices, electronics, photonics, optoelectrical detectors, solar cells, fuel cells, light emitting diodes, fluorescent agents, photocatalysis, and lithium-ion batteries (Yan *et al*., 2010; Son *et al*., 2012; Tsai *et al*., 2015; Zhu *et al*., 2015; Park *et al.,* 2016; Zheng and Wu, 2017; Tian *et al*., 2018; Oluwafemi, 2019).

Owing to its versatility in commercial applications, the preparation of high-quality GQDs on a mass scale and improving their functional properties have gained great attraction in the recent past (Figure 2). Due to the ability of opening a bandgap, up conversion and down conversion engineering, and other promising features, GQDs have led to the improvement in commercial applications such as optoelectronics, energy conversion and storage devices (like organic photovoltaics, sensitized electrochemical solar cells, batteries, supercapacitors) as well as emerging biomedical applications such as nanocarriers in drug delivery, cancer therapy, antibacterial, and bioimaging and sensors (namely luminescence chemosensors, electrochemical chemosensors, and biosensors). GQDs have paved the way to gain exceptional efficiency enhancement in photophysical devices. In the field of nonlinear optics and quantum computing, some interesting novel applications of GQDs have been reported very recently (Banszerus *et al*., 2020; Danial *et al*., 2022).

**Corresponding Author's Email:* awijendr@yahoo.com
https://orcid.org/0000-0003-1659-3042

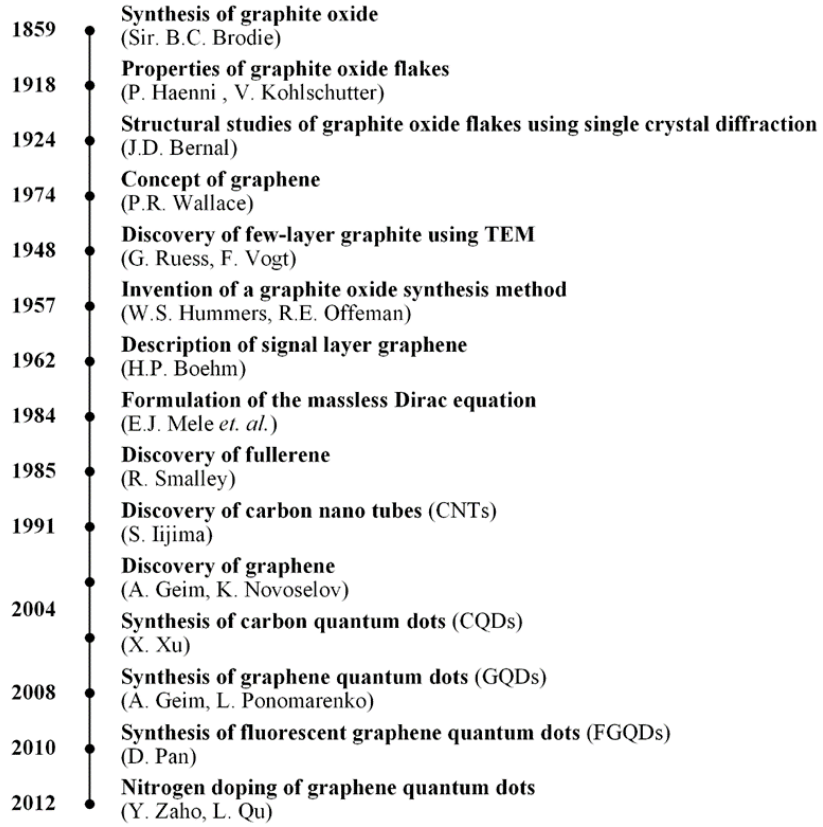

Figure 1: The timeline of the development of functional carbonaceous materials and related theory (Tian *et al.,* 2018).

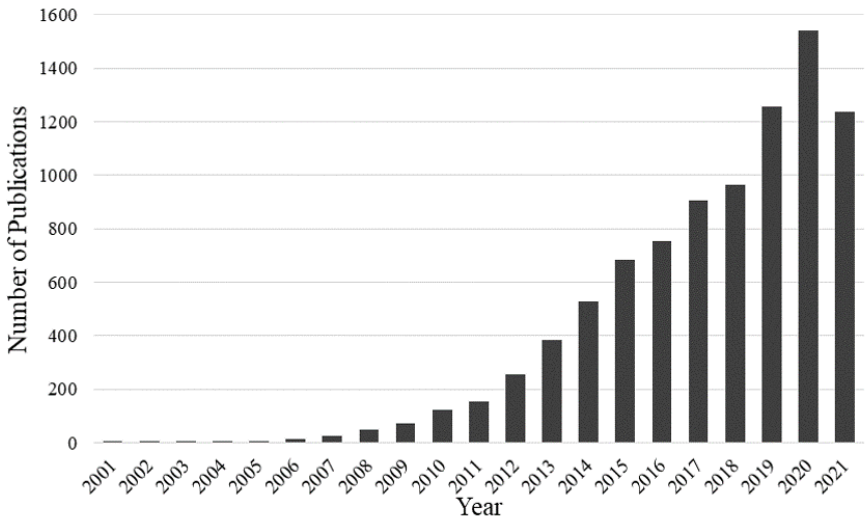

Figure 2: The number of publications in the period 2001-2021 containing the word "graphene quantum dots" in the title, abstract, or keywords. Data source: Scopus (26th Aug 2022).

Quantum dots and their applications

The unique properties of dimensionally confined nanoparticles are already being used in a range of applications. These nanoparticles are also known as artificial atoms or quantum dots (QDs) due to the splitting of energy bands (or quantization of energy bands) (Bandara *et al*., 2023). The underlying behavior of QDs can theoretically be understood via the quantum confinement phenomena. However, QD size is material-dependent since the exciton Bohr radius depends on the type of the material. The optical and electrical properties of such structures can be optimized in order to enhance the performance in various applications by fine-tuning the size, shape, structure (for example, core-shell configuration), and by attaching functional groups (Kittiratanawasin and Hannongbua, 2016). QDs are also used in energy conversion and storage devices (Bandara *et al*., 2018; Bandara *et al*., 2020). QDs are already a well-established technology in commercial light-emitting diodes (LEDs), display applications,

photoconductors, photocatalysis, and sensors (Lim *et al*., 2015; Cotta *et al*., 2020). In addition, QDs are incorporated in research on supercapacitors, photoelectrochemical H_2 generation and secondary batteries. Further, they are utilized in biotechnology biomonitoring, drug delivery and luminescence (Molaei *et al*., 2019).

Size of a quantum dot and tuning the bandgap

A significant number of studies can be found on synthesizing GQDs with two-dimensional lateral sizes less than 100 nm (Li *et al*., 2015; Bak *et al*., 2016; Chen *et al*., 2018). Also, several authors have reported three-dimensional multilayer (i.e., less than 10 layers) GQDs with sizes less than 10 nm (Liu *et al*., 2011; Kittiratanawasin and Hannongbua, 2016; Choi, 2017). In principle, to be labeled as a 'dot,' any type of quantum dot should be functionally zero-dimensional. That is, to become a quantum dot, the particle should exhibit quantum confinement phenomena regardless of the geometrical dimensions, as elaborately explained in Bandara *et al*., 2023. A GQD can even have different shapes. For example, 2-D nanostructures can be triangular, tetragonal, polygonal, or circular, while 3-D structures can be prismatic, conical, trapezoidal, cubic, or spherical. Thus, defining a GQD using geometrical features such as lateral dimensions, thickness, shape, or number of layers along is not very meaningful. However, the bandgap of a pure GQD is inversely proportional to the geometrical dot size, and some properties of a GQD can be engineered by varying the size and geometry (Zacharias et al., 2020; Zacharias *et al*., 2021). Moreover, the bandgap of a GQD can also be tuned by doping or attaching functional groups and heteroatoms. Quite a significant bandgap variation can be achieved by changing these attributes (Tang *et al*., 2013; Das *et al*., 2015; Zhu *et al*., 2015; Wang *et al*., 2016a; Chen *et al*., 2018). In this short review, the reliable GQD fabrication techniques to date are discussed, emphasizing the synthesis requirements, strengths, weaknesses, and specialties of each technique.

Synthesis workflow of graphene quantum dots

Generally, there are two main approaches to synthesize GQDs; bottom-up and top-down (Zhang *et al*., 2019). In the bottom-up approach, carbon atoms sourced from a microscopic precursor material are aggregated into single or multilayer graphene sheets of finite size with atomically precise control. On the other hand, in the top-down approach, macroscopic precursor materials like bulk graphite are used in the initial step. Then, the graphite is exfoliated to graphene by breaking inter-layer van der Waals bonds. GQDs are formed by simultaneously or subsequently cutting down the separated layers. Further, in the top-down approach, other low-dimensional carbon-based hexagonal crystalline structures, such as carbon nanotubes or fullerenes, can also be cut down or fragmented to GQDs (Lu *et al*., 2011).

In any approach, the usual synthesis workflow is as follows; A precursor is treated with other reagents under suitable experimental conditions (temperature, pressure, atmosphere, and pH). The energy required to re-organize the bonds is usually given as heat and/ or mechanical, chemical, or electrochemical means. Next, the products are purified and finally characterized before being used in applications. On top of the chemical procedures, physical methods such as sonication, microwaves, and electrochemical methods can be used as alternate or assistive techniques of GQD synthesis.

As the **precursor,** natural or pre-synthesized carbon-rich materials are used. In bottom-up synthesis, precursors will be small carbon-based molecules such as citric acid, sucrose, or gases such as methane. For top-down approaches, carbonaceous structures such as graphene sheets, graphene oxide (GO), carbon nanostructures (tubes, rods, fullerenes, etc.), or even some natural mineral products like graphite and coal can be used. Most chemical methods employ an aqueous reaction **medium**. GQDs synthesized in such media usually have hydrophilic surface functional groups like carboxylic acid and aldehyde (Bandara *et al*., 2022a). Alternatively, by using solvents other than water, organic-soluble GQDs can be synthesized with desired functional groups (Kwon *et al*., 2014).

Purification of GQDs or isolating the products of the desired size is usually the most inefficient and time-consuming part and is a significant hurdle for commercialization and mass production. Sonication is generally used in loosening up the products. In some methods, neutralizing pH is a necessity before purification. In the case of volatile solutions or dispersants, evaporation is a straightforward approach, while in the case of aqueous solutions, ethanol is added to promote precipitation. After the pre-treatment, intermediate filtration might be necessary by means of vacuum filtering, slow filter papers, or coarse (polytetrafluoroethylene) membranes. In most techniques, the final GQDs are isolated using membrane dialysis using standard dialysis bags usually made of the regenerated cellulose ester. Despite dialysis being the most popular GQD isolation strategy in research, centrifugation and chromatography also can be used.

Once synthesized and isolated, GQDs can be **characterized** using multiple techniques. Among those, the standard technique used to compare yield between different synthesis methods is photoluminescence spectroscopy (PL). These probes are summarized in Table 1, and many other techniques can also be used in further characterizing graphene and GQDs, as extensively discussed in Zhang *et al*., 2019, Bandara *et al*., 2022a, and the references therein.

Bottom-up approaches

Carbonization

Carbonization (a.k.a. pyrolysis) techniques constitute a prominent class of bottom-up GQD synthesis. There are several approaches to carbonization, namely hydrothermal, solvothermal, and electrochemical synthesis.

In the hydrothermal approach, two sources of carbon and nitrogen are dissolved in water. Citric acid ($C_6H_8O_7$) and urea ($(NH_2)_2CO$) are common reagents. In

an autoclave of about 1 MPa pressure, the solution is kept at a suitable temperature for up to 180 mins. This method has resulted in GQDs incorporated with N – atoms and the photoluminescence intensity of the samples were found to be dependent on the C–N configuration (Permatasari *et al*., 2016).

A faster method is microwave-assisted hydrothermal synthesis (Figure 3). Here, a microwave source is used to heat the solution in a tightly sealed container. The tunable parameters of this approach are microwave power, heating time, precursor concentration, and solution volume. Membrane dialysis is then used to separate the QDs. Using the glucose precursor, GQDs of photoluminescence quantum yields up to 11% have been obtained in this way (Tang *et al*., 2012). The microwave-assisted method has also been used to synthesize nitrogen-doped multilayer (3 to 10 layer) GQDs, with glucose and urea seed solutions (Hou *et al*., 2016). The PL yield reported for this case is 5.2 %.

A combination of hydrothermal and solvothermal approaches can be used in synthesizing doped GQDs. Citric acid (C source), mixed with urea (N source) or thiourea (N and S source), is heat treated in an autoclave to obtain N- doped or N, S co-doped GQDs [B-26]. These doped samples have delivered quantum yields as high as 78%. Pyrrolic nitrogen-doped pN-GQDs have also been

Table 1: Experimental techniques for Graphene and GQD characterization (Zhang et al., 2019).

	Acronym	Technique	Key Measurement
1	SEM	Scanning electron microscopy	Surface images, particle size
2	TEM	Transmission electron microscopy	High-resolution images / diffraction
3	STM	Scanning tunneling microscopy	Surface images, electron density, morphology
4	AFM	Atomic force microscopy	Thickness and morphology
5	Raman Spectroscopy		Defects, layer count, quality of the product
6	PEEM	Photoemission electron microscopy	(real-time) fast processes
7	LEEM	Low-energy electron microscopy	(real-time) thickness
8	LEED	Low-energy electron diffraction	fast processes
9	XRD	X-ray diffraction	Crystalline structure, particle size
10	XPS	X-ray photoelectron spectroscopy	Elemental analysis, bonding
11	UV-Vis	Ultraviolet-visible spectroscopy	Chemical concentration / composition, optical properties
12	BET	Brunauer–Emmett–Teller surface area analysis	Surface area /porosity
13	TGA	Thermogravimetric analysis	Thermal stability/decomposition
14	NMR	Nuclear magnetic resonance	Atomic properties
15	FTIR	Fourier transform infrared spectroscopy	Chemical composition / bonding
16	PL	Photoluminescence spectroscopy	Optical properties/ yield

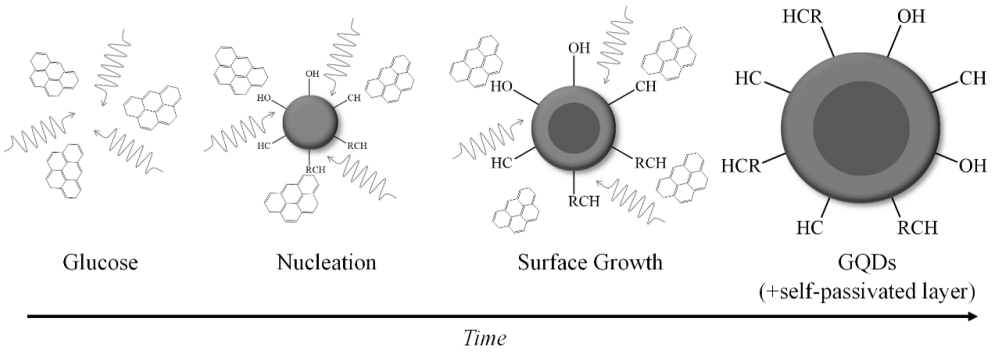

Figure 3: Microwave-assisted hydrothermal synthesis of graphene quantum dots from glucose precursor (Tang *et al*., 2012).

synthesized using similar precursors but in a solvent like DMF (Noor *et al*., 2018). This process is outlined in Figure 4. A range of sizes and a spectrum of emitted colors have been observed by varying the concentration of pyrrolic nitrogen. The controllable polydispersity might be useful in fabricating white LEDs.

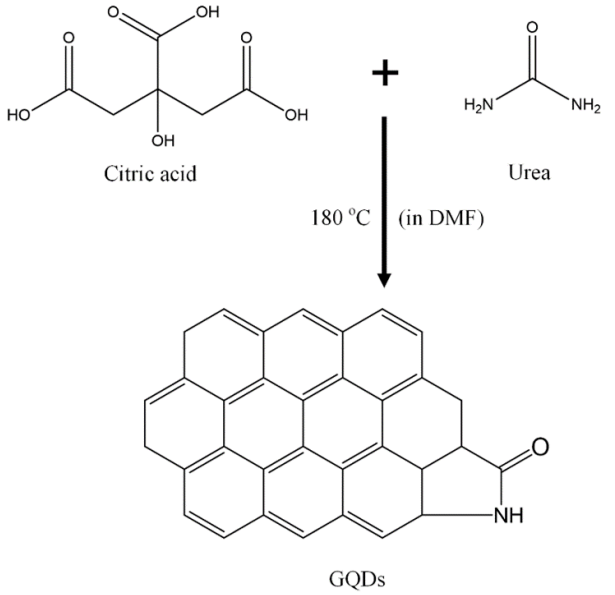

Figure 4: Solvothermal synthesis of pyrrolic nitrogen-doped GQDs (pN-GQDs), starting from citric acid (carbon source) and urea (nitrogen source) (Noor *et al*., 2018).

In the electrochemical carbonization approach, an electrochemical cell with working and counter electrodes is used. These electrodes are usually inert platinum sheets. Optionally, a third reference electrode, such as a calomel electrode, can be added to the system. Generally, the size of the QDs increase with the applied potential. In a preliminary report, low-molecular-weight alcohol was used with water and NaOH, leading to a 15.9% quantum yield (Deng *et al*., 2014). Modifications to this electrochemical carbonization have been tested with graphite electrodes and citric acid introduced to the electrolyte.

Soft template method

Soft templates can be used to produce capped colloidal QDs. The size can be easily manipulated. In such a report (Kwon *et al*., 2014), a carefully controlled mixture of oleylamine and octadecene was injected into an aqueous mixture of citric and nitric acid. The resultant emulsion was heated, precipitated (using ethanol), centrifuged, repeatedly dispersed (using hexane), and vacuum dried. The resulting organic-soluble oleylamine capped colloidal QDs have shown a quantum yield of 60 %.

Chemical vapor deposition

The standard CVD technique of fabricating graphene has been modified to synthesize GQDs. In an argon atmosphere, a heated (~1000 °C) substrate in a quartz reaction tube is purged with hydrogen and methane (as the source of C). Subsequent cooling of the substrate results in GQDs that are transferable to different substrates. By changing the CH_4:H_2:Ar ratio, GQDs with different thicknesses can be produced. As the substrates, polycrystalline copper (Ereš and Hrabar, 2018), hexagonal boron nitride (Ding, 2014), and metal-based nickel alloy ($MmNi_3$) (Saroja *et al*., 2020) have shown promising results. In CVD, the controllable parameters are the precursor composition, catalytic properties of the substrate, gas flow rates, pressure, and reaction time.

Top-down approaches

Modified Hummers method (synthesis of reduced graphene oxide)

Reduced graphene oxide (rGO) is used as the starting substance for most top-down GQD synthesis methods (Wu *et al*., 2009; Dutta et al., 2012; Zhang *et al*., 2019; Bandara *et al*., 2022a). It is worth briefly outlining the modified Hummers method (MHM), which is the prominent technique for synthesizing rGO. First, chunks of graphite are mechanically ground to a powder. This powder is then stirred with sodium nitrate, sulfuric acid, and potassium permanganate to produce graphite oxide. Then water is added and ultrasonicated in order to promote exfoliation. Centrifugation will then separate the unreacted graphite. Next, the graphite oxide dispersion is mixed with water and hydrazine to produce graphene oxide (GO). Reduction agents are then added to reduce the GO while heating is controlled (Mao *et al*., 2011; Pei and Cheng, 2012; Lesiak *et al*., 2021). Applicable reduction agents are; aqueous ammonia, ascorbic acid, borohydride, formaldehyde, sodium hydroxide, potassium hydroxide, hydrazine and hydrazine derivatives, sodium hydride, sodium borohydride, hydroiodic acid, ascorbic acid, hydroquinone, pyrogallol, hydroxylamine or urea. Reduction procedures can be conducted under different conditions (such as using vapor or aqueous solutions of different concentrations and times) would result in slightly altered chemical and structural properties of rGO.

The key challenge is moving toward greener synthesis methods and avoiding the use of harsh chemicals in the process of oxidation and reduction. In addition, the complete reduction of rGO to graphene is not easily achieved, and it is an open challenge for researchers to go beyond partial reduction. Despite the existence of alternative methods like electrochemical exfoliation, MHM remains the most common initial step for top-down GQD preparation.

Mechanical exfoliation

In simple terms, a QD is just a very tiny object. We can imagine breaking down a chunk of macroscopic graphite to the required size by pure physical (mechanical) degradation. But this simple task remained a challenge until recently, yielding to a monopoly of chemical methods. However, it has been shown that some straightforward, scalable, and commercializable mechanical methods like ball-milling can produce GQDs. Recently, carbon nanocapsules of size 20 ~30 nm have been used as a precursor, while sodium

carbonate acted as an intercalation agent in a zirconia ball mill (Lomeda *et al*., 2008). The precursor: intercalation agent ratio is an optimizable parameter toward the yield.

Hydrothermal cutting

Chemically cutting down of graphene sheets or GO sheets can be done in several different methods. The following procedure was used in the first report (Pan *et al*., 2010). First, GO sheets were produced by the modified Hummers method, and then they were baked in a nitrogen environment to promote thermal deoxidization. Next, concentrated H_2SO_4 and HNO_3 acids were used in oxidation. Then functional groups like CO/COOH, OH, and C-O-C were attached to make the graphene sheets water-soluble. Thereafter, the pH value of the solution was adjusted to 8 by adding NaOH. Next, the mixture was annealed in an autoclave, followed by membrane-assisted micro filtration once cooled down to room temperature. As the final step, the resultant colloidal suspension was dialyzed. The authors have amounted this process to the hydrothermal cutting of epoxy and carbonyl groups (Figure 5). Since the initial study, this hydrothermal route has been improved by utilizing well-ordered GO sheets processed at higher temperatures and in a strongly alkaline environment (Pan *et al*., 2012).

Continuous hydrothermal flow synthesis is an alternative approach that can be relatively simple and fast using non-toxic reagents. In one such flow method (Kellici *et al*., 2017), an aqueous solution of GO and calix[4]arene tetrasulfonic acid (SCX4) was mixed with KOH at room temperature. Next, in a reactor at 24.1 MPa, the above flow was brought into contact with supercritical water at 450 °C and subsequently cooled to obtain GQDs. This process is schematically illustrated in Figure 6.

Solvothermal synthesis

Here, organic solvents such as dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) are used in place of water. By using DMF (Zhu *et al*., 2011), a quantum yield of 11.4% has been reported. Interestingly, the resultant GQDs were soluble in a range of solvents like water, DMF, ethanol, tetrahydrofuran, acetone, and DMSO. This has been accounted to the presence of functional groups such as epoxy/ether,–OH, =C=O, and $–CO–NR_2$, which are decomposition fragments of the solvent (DMF) itself. A cost-effective solvothermal process has been demonstrated using graphite as the precursor, DMF as the solvent, and hydrogen peroxide as the oxidant (Tian *et al*., 2016). This process is briefly outlined in Figure 7.

Chemical (oxidative) exfoliation

Some bonds between carbon atoms can be cut by using strong oxidative agents like HNO_3 and H_2SO_4 on graphene, GO, or carbon nanotubes. A series of methods, such as oxidative cleaving/cutting, acidic oxidation, and chemical exfoliation, come under this class. These methods are straightforward and common, nevertheless yielding higher quality GQDs. The general procedure is as follows. First, the precursor is treated with a mixture of concentrated acids (H_2SO_4 and HNO_3, or $HClO_4$) and sonicated. Then the product is stirred at a suitable temperature for an extended time. Next, it is cooled down to room temperature, and pH is adjusted to 7~8 by adding NaOH, Na_2CO_3, etc. GQDs can then be purified using dialysis and evaporation.

A range of carbonaceous precursor materials have been tested, such as pitch-based carbon fibers (Peng *et al*., 2012), GO (Maiti *et al*., 2017), anthracite coal, bituminous

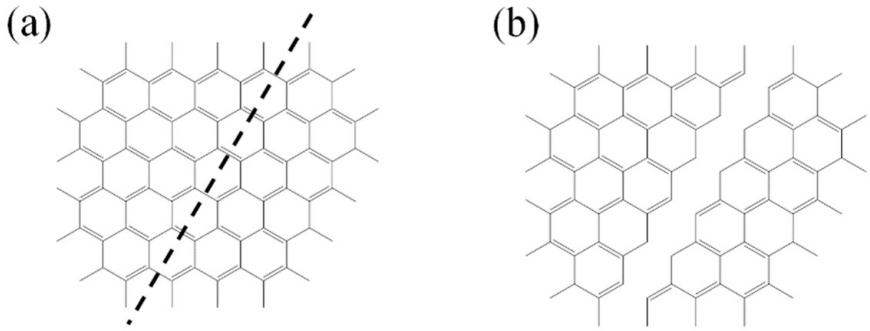

Figure 5: Hydrothermal cutting (deoxidization) of graphene. (a) before, and (b) after (Bandara *et al*., 2022a).

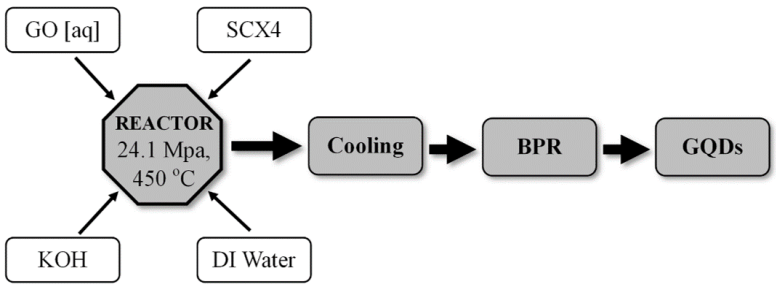

Figure 6: Flowchart of the continuous hydrothermal flow synthesis of graphene quantum dots from graphene oxide (GO) and calix[4] arene tetrasulfonic acid (SCX4) (Kellici *et al*., 2017; Bandara *et al*., 2022a).

coal, and coke (Ye *et al*., 2013). It has been observed that the photoluminescence intensities, size, and morphology of GQDs change with the choice of precursor material.

Fullerene fragmentation

Buckminster fullerenes (C_{60}), carbon nanotubes, and other layered carbon structures can be fragmented into graphene and GQDs. Room temperature sputtering of argon ions onto catalyst crystals and subsequent annealing have been tried in an ultra-high vacuum (UHV) environment (Lu *et al*., 2011). The surface vacancies of a catalytic crystal, such as ruthenium, embed fullerene molecules and fragment them once the temperature increases. The diffusion and aggregation of these fragments form GQDs, and the results seem very sensitive to the annealing temperature.

Ultrasonic exfoliation

Ultrasonication is a technique used with several GQD synthesis methods. It can be used to exfoliate the graphite planes or to remove trapped air in liquid phase synthesis. Ultrasonic-assisted exfoliation from the liquid phase can be used to produce GQDs as a standalone method as well. This approach has some control over the defects.

In such a study (Hassan *et al*., 2013), the acetylene-black precursor was used with N-methyl-2-pyrrolidone (NMTP) solvent under mild ultrasonication, followed by liquid phase dispersion and centrifugation. Repeating this procedure has gradually replaced the acetylene black with nano-graphite. In some other studies, the ultrasonic technique has been extended using platelet graphite nanofiber precursors (Shih *et al*., 2014) and microwave-assisted expansion (Zdrazil *et al*., 2018).

Electrochemical synthesis

In an electrochemical cell, a carbon-rich source (graphite, GO, carbon nanotubes, etc.) is used as an expendable electrode, along with a platinum counter electrode (Bandara *et al*., 2022b; Wickramasinghe *et al*., 2022). The resulting expanded graphite can further be separated to form graphene or GQDs. A reference electrode can also be used to control and measure the potentials. A wide range of electrolytes have been studied. For example, carbon paper covered with multiwalled carbon nanotubes (MWCNTs) placed in a Teflon jacket has been used as the electrode along with a degassed acetonitrile electrolyte with 0.1 M tetrabutylammonium perchlorate (TBAP) (Li *et al*., 2013). In another study (Nasibulina *et al*., 2010), a glassy carbon electrode covered with GO was used with an electrolyte solution of $LiClO_4$ in propylene carbonate (Figure 8).

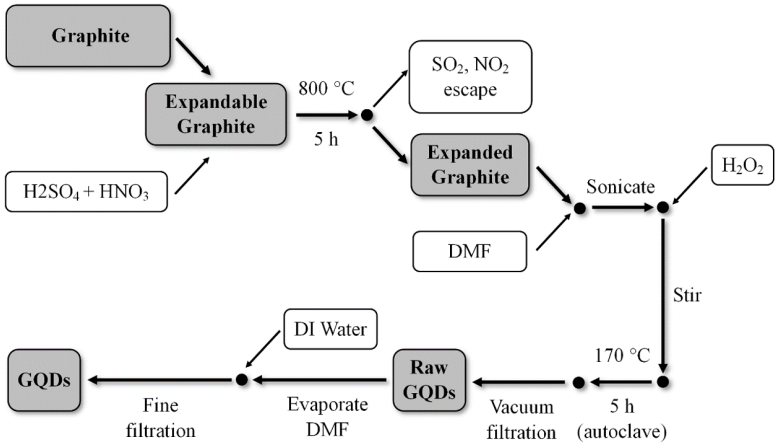

Figure 7: Flowchart of the solvothermal synthesis of graphene quantum dots from graphite using hydrogen peroxide as the oxidant (Tian *et al*., 2016; Bandara *et al*., 2022a).

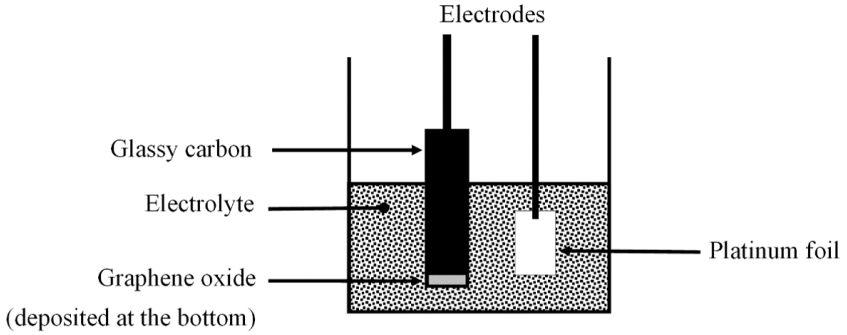

Figure 8: Electrochemical cell for extracting graphene oxide from bulk glassy carbon (Nasibulina *et al*., 2010).

Table 2: Summary of Graphene quantum dot synthesis methods.

#	Method	Precursor	Reagents	Approx. Time*	PL Yield %	Notes	References
			Bottom-up approaches				
1	**Hydrothermal carbonization**	citric acid	water, urea	2 h (+P.T.)	--	under pressure	Permatasari *et al*., 2016
2	**Microwave-assisted hydrothermal carbonization**	glucose	water, urea	10 min (+72 h)	5 ~ 11	faster (min scale, before purification)	Zhu *et al*., 2009; Zhai *et al*., 2012; Tang *et al*., 2012; Choi, 2017
3	**Hydrothermal carbonization (doped GQDs)**	citric acid	water, thiourea, ethanol	8 h (+P.T.)	71~78	high yield	Qu *et al*., 2013; Son *et al*., 2006
4	**Solvothermal carbonization (doped GQDs)**	citric acid	DMF, urea	--	--	controllable size	Noor *et al*., 2018
5	**Electrochemical carbonization**	alcohol (low molecular weight)/ citric acid	water, NaOH, ethanol (Pt electrode)	4h+24h (+P.T.)	15.9	controllable size	Deng *et al*., 2014; Ahirwar *et al*.,2017
6	**Soft template method**	citric acid	water, nitric acid, ethanol, hexane	2h (+P.T.)	60	high quality/ controllable size	Zhang *et al*., 2019
7	**Chemical vapor deposition (CVD)**	methane	argon, hydrogen (polycrystalline copper)	--	--	costly	Ereš and Hrabar, 2018; Fan *et al*., 2013; Ding, 2014; Saroja *et al*., 2020;
			Top-down approaches				
1	**Mechanical exfoliation (Ball milling)**	carbon nanocapsules	Na_2CO_3	4 (+24)	--	commercializable	Lomeda *et al*., 2008
2	**Hydrothermal cutting**	GO sheets	H_2SO_4, HNO_3 (Acids)	12 h (+P.T.)	--	ultra-fine	Sharma, 2020; Pan *et al*., 2012
3	**Continuous hydrothermal flow synthesis**	GO	calix[4]arene tetrasulfonic acid, KOH	N/A	--	high pressure, commercializable	Wang *et al*., 2016b
4	**Solvothermal Synthesis**	expandable graphite	DMF, DMSO H_2O_2	10 h (+P.T.)	11.4	good solubility, high purity	Zhu *et al*., 2011; Tian *et al*., 2016
5	**Chemical Exfoliation**	graphene/ GO/ carbon nanotubes /Carbon fiber/Coal	H_2SO_4, HNO_3 / $HClO_4$ (Conc. Acids), Na_2CO_3/ NaOH	26 h (+P.T.)	14 [B-11]	slow dialysis	Peng *et al*., 2012; Ye *et al*., 2013; Maiti *et al*., 2017
6	**Fullerene Fragmentation**	Buckminsterfullerene (C_{60})	(ruthenium crystals)	--	--	--	Lu *et al*., 2011

							Lu *et al*., 2016;
7	**Ultrasonic Exfoliation**	acetylene black/ platelet graphite nanofibers/ expandable graphite	N-methyl-2-pyrrolidone / dimethyl sulfoxide	--	--	control over defects	Hassan *et al*., 2013; Shih *et al*., 2014; Zdrazil *et al*., 2018
8	**Electrochemical synthesis**	multiwalled Carbon nanotubes/ GO	tetrabutylammonium perchlorate (TBAP) / $LiClO_4$, propylene carbonate (Pt electrodes)	--	low	--	Li *et al*., 2013; Nasibulina et al., 2010
9	**Nanolithography**	graphene	(Si substrates, polymethylmethacrylate (PMMA) masks)	--	low	costly	Ponomarenko *et al.,* 2008; Wang et al., 2012

Nanolithography

This is an expensive technique with a lower yield, but worth discussing. High-resolution electron-beam lithography has been used to cut graphene to smaller shapes and sizes ~ 10 nm (Ponomarenko *et al*., 2008). Polymethylmethacrylate (PMMA) is often used as a mask. Standard electron-beam lithography and oxygen plasma etching with PMMA masks have also been used to carve out double QDs from graphene sheets placed on silicon substrates (Wang *et al*., 2012).

Summary of GQD synthesis methods

Table 2 summarizes the GQD synthesis methods discussed above. In general, the time required for the synthesis is shorter in the case of bottom-up approaches when compared to top-down approaches. However, in both approaches, a significantly longer time is necessary for the subsequent purification (P.T.) than the synthesis itself. Depending on the demand parameters such as size, purity, and yield, several different purification options for each synthesis method might be applicable. Note that this information is predominantly research-based, and neither yields nor time scales have been optimized for commercial implementation. If mass production is intended, these processes have room for efficiency enhancement and speedup.

Challenges of synthesis and future prospects of GQDs

In both approaches to GQD synthesis, there are inherent challenges as well as prospects. In the bottom-up approach, the fundamental challenge is to assemble carbon atoms in the two-dimensional graphene structure since carbonaceous structures can assume many other forms. On the contrary, for the top-down approaches, isolating single (or a few) layers of graphene is challenging (Kellici *et al*., 2017).

Methods requiring strong acids, bases, toxic chemicals, and corrosive reagents are harmful to the environment and expensive to handle in a commercial setting. At the same time, high-pressure /temperature and vacuum-based techniques can have a higher energy demand. Further, commercialization demands continuous flow techniques over batch processing. Another challenge is adopting environmentally friendly synthesis methods. For example, harsh acids, toxic chemicals, and byproducts come with disposal issues. Therefore, future research should pay more attention into inventing greener synthesis methods that give high yields and are suitable for defects-free mass production of GQDs.

Synthesis methods using water-based solvents and reagents are commercially cheaper and can be environmentally friendly. On the other hand, the use of volatile organic solvents and inorganic reagents leads to relatively pure GQDs. Also, the base (high pH) medium plays a vital role in activating surface functional groups attached to the GQDs. This, with edge effects, determine the solubility and other vital properties. However, solubility can be controlled by explicitly binding organic functional groups during or after preparing the GQDs (Kwon *et al*., 2014).

The use of advanced and costly setups like CVD and lithography are challenging in commercially scalable mass production and are currently reserved only for synthesizing GQDs with specialized requirements. The preparation of GQDs with high purity, along with controlled shapes and sizes, is possible with these methods. However, mass-scale low-cost synthesis using the techniques like CVD and lithography are yet to be realized.

Since GQDs are used in a multitude of applications, the optimization of specific functional properties for each application should be separately done by controlling the edge effects, type and number of functional groups, composition and type of composites and dopants, size, and shape. Low quantum yield and weak PL response of GQDs are problematic in many methods. Depending on the application, doping can be used as a compensation since GQDs dope with metal, non-metal, or organic molecules have shown improved optical and electronic properties (Son *et al*., 2006; *Qu et al*., 2013; Noor *et al*., 2018). Electrochemical synthesis techniques (in both top-down and bottom-up approaches) have the potential for commercialization, but their photoluminescence yield is not appreciable to date. For a country with resources like natural graphite, top-down approaches are generally suitable for mass production.

As mentioned above, the popular top-down GQD synthesis approach uses rGO. This method is not suitable for the fabrication of pristine graphene or GQDs. The complete reduction of GO to graphene is still an unresolved challenge for the researchers though the partial reduction to rGO along with high yields has been achieved using various methods and precursors. Future research on GO-based techniques should mainly be focused on; (a) achieving precise control over the oxidation of graphite, (b) going beyond partial reduction and finding a method that can be adapted for the complete reduction of GQDs, (c) controlling functionalization that can alter the desired properties of GQDs, (d) obtaining high-yield of non-defective graphene and GQDs (Pei and Cheng, 2012), (e) innovating scalable, quick and greener synthesis methods toward commercialization.

In any top-down or bottom-up method on a research scale or in commercial mass-production, the purification of GQDs remains the most time-consuming and inefficient step. The popular membrane dialysis technique is very slow and thus not commercially viable. Therefore, the improvement and innovation of quantum dot purification techniques to overcome this bottleneck will be the most critical step toward the next carbon-based revolution.

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DECLARATION OF CONFLICT OF INTEREST

The authors declare no competing interests.

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