Weifeng Chen, Guo Lv, Weimin Hu, Dejiang Li, Shaona Chen* and Zhongxu Dai* Synthesis and applications of graphene quantum dots: a review

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Abstract: As a new class of fluorescent carbon materials, graphene quantum dots (GQDs) have attracted tremendous attention due to their outstanding properties and potential applications in biological, optoelectronic, and energy-related fields. Herein, top-down and bottom-up strategies for the fabrication of GQDs, mainly containing oxidative cleavage, the hydrothermal or solvothermal method, the ultrasonic-assisted or microwave-assisted process, electrochemical oxidation, controllable synthesis, and carbonization from small molecules or polymers, are discussed. Different methods are presented in order to study their characteristics and their influence on the final properties of the GQDs. The respective advantages and disadvantages of the methods are introduced. With regard to some important or novel methods, the mechanisms are proposed for reference. Moreover, recent exciting progresses on the applications of GQD, such as sensors, bio-imaging, drug carriers, and solar cells are highlighted. Finally, a brief outlook is given, pointing out the issues still to be settled for further development. We believe that new preparation methods and properties of GQDs will be found, and GQDs will play more important roles in novel devices and various applications.

Keywords: bottom-up; graphene quantum dots; photoluminescence; quantum confinement effect; top-down.

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1 Introduction

Graphene, discovered by Novoselov et al. in 2004 [1], is a new kind of nanomaterial with excellent mechanical, electrical, thermal, and optical properties [2–5], following the zero-dimensional fullerenes [6, 7] and the one-dimensional carbon nanotubes [8–11]. Many synthesis methods have been developed, such as micromechanical stripping [1, 12], chemical vapor deposition (CVD) [13–15], SiC epitaxial growth [16–18], and graphene oxide (GO) reduction [19, 20]. Because of the large plane conjugate structure of graphene, the π electrons have a significant delocalization effect. As a result, graphene possesses a zero band gap which is the feature of half-metallic materials, limiting its application in the fields of optoelectronic devices and semiconductors [21].

Graphene quantum dots (GQDs), which are small pieces of graphene with a two-dimensional lateral size (less than 100 nm), have been developed in recent years [22-24]. Strictly speaking, ideal GQDs have a single atomic layer and only contain carbon. Actually, most of the prepared GQDs also contain oxygen and hydrogen, and often have multiple atomic layers, with sizes being less than 10 nm [25, 26]. The band gap energy of the GQDs can be regulated from 0 to 6 eV by changing the two-dimensional size or surface chemical properties, due to the quantum confinement effect of conjugated π -domains and the edge effect [27–30]. High-resolution transmission electron microscopy (HRTEM) observations show that the GQDs have the hexagonally symmetrical crystalline structure, and the in-plane lattice spacing is 0.24 nm, completely the same with graphene [31–33]. Fourier transform infrared (FT-IR) spectroscopy and X-ray photoelectron spectroscopy (XPS) tests demonstrate that the hydrogen and oxygen in the GQDs mainly exist in the form of oxygencontaining groups, such as hydroxyl, carbonyl, carboxyl, and epoxy groups [32, 34]. At present, a lot of research work is devoted to the surface chemical modification of the GQDs in order to regulate the properties for the applications [35–37]. The main approaches involve the control of oxidation degree [38–41], surface functionalization [35, 42–44], and heteroatom doping [32, 45–47].

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Compared to the quantum dots of a traditional semiconductor, the GQDs possess many advantages, such as stable fluorescence properties [48-51], low toxicity [40, 52–54], and good water solubility [55, 56]. Among them, the fluorescence properties are the most important feature of the GQDs. Although the photoluminescence (PL) mechanism of the GQDs can be explained by the size of the GQDs, surface chemical groups, and doping atoms, there is no universal agreement on the specific PL mechanism. The dominant PL mechanism of GQDs consists of the quantum confinement effect of conjugated π -domains, the surface/edge state in GQDs, as well as the synergistic effect of these two factors [57]. Their fluorescent emission wavelength can be in various regions, including deep ultraviolet light [49], blue light [50, 51], green light [39, 58], yellow light [52, 59], and red light [27, 60]. It is attributed to the different sizes, surface functional groups, and excitation wavelength.

Besides, though the GQDs synthesized by various methods have different ultraviolet-visible absorption characteristics, the π - π * transition absorption peak ranges commonly from 200- to 270-nm wavelength, and the n- π * transition absorption peak is more than 260 nm [55, 59]. The ultraviolet-visible absorption is dependent on the size of the GQDs, due to the quantum confinement effect [31, 61]. In addition, oxygen-containing functional groups on the surface of the GQDs also have an important influence on the absorption peak position [62].

Moreover, GQDs have a better potential application in biological medicine than graphene or GO, attributed to the smaller two-dimensional nanosize [63]. Naturally, the biocompatibility and toxicity of GQDs are the major concerns. There has been some research that indicate that GQDs have relatively good biocompatibility and low biological toxicity [40, 52–54, 64]. In addition, GQDs have a single atomic layer plane conjugate structure, a large specific surface area, and oxygen-containing groups on the surface, which can provide the active sites, easily carrying or loading drug molecules. Therefore, GQDs possess some unique properties different from graphene and GO. To date, there have been several reviews about GQDs, due to the significance and urgency of the research on them. For instance, Li et al. [65] introduced potential methods like acid oxidation, hydrothermal and solvothermal reactions, etc. for the preparation of GQDs. They emphatically discussed four representative types of biomedical application based on GQDs, bioimaging, biosensing, drug delivery, and antimicrobial materials in detail. Li et al. [66] summarized the synthetic methods on the top-down routes, which possess the advantages of abundant raw materials, large-scale production, and simple operations, and

systematically discussed the optical properties of GQDs, ranging from the mechanism and the influencing factors to the optical tunability. This work will be very useful in quickly gaining knowledge and experience in creating novel functional GQD-based nanomaterials for further applications in biomedicine, materials science, analytical science, and optical nanodevices.

In this article, the latest research progresses on the preparation and applications of the GQDs are reviewed. Top-down and bottom-up strategies, which mainly contain oxidative cleavage [34, 67], the hydrothermal or solvothermal methods [68, 69], ultrasonic-assisted or microwave-assisted processes [70, 71], electrochemical oxidation [72, 73], controllable synthesis [74], and carbonization [75, 76] from small molecules or polymers, are discussed. Different methods are presented in order to study their characteristics and the influence on the final properties of the GQDs. The respective advantages and disadvantages of the methods are introduced. The mechanisms of some novel methods are proposed for reference. Additionally, the potential applications of the GQDs, such as sensors, bio-imaging, drug carriers, and solar cells are comprehensively introduced. Finally, a brief outlook is given, pointing out the issues waiting to be settled for further development. The current review demonstrates that the GQDs exhibit superior performances and will be applied in many fields of new materials and novel devices.

2 Synthesis methods of GQDs

In detail, the synthesis methods of the GQDs can be classified into two categories: top-down strategy and bottom-up strategy (as shown in Figure 1) [57]. The former is extensive in the synthesis of GQDs because it is simple and effective. GQDs are gained from carbon materials, including graphene, fullerenes, carbon nanotubes, etc., by cutting them via chemical or physical methods, such as oxidative cleavage, hydrothermal or solvothermal method, electrochemical oxidation, ultrasonic-assisted or microwaveassisted process, chemical vapor deposition (CVD), and laser ablation. For the latter, GQDs are fabricated through controllable synthesis or carbonization from suitable organic molecules or polymers. The controllable synthesis is precise but complicated, needing many steps of synthesis to obtain GQDs of large dimension. In the carbonization method, GQDs are obtained from suitable small molecules or polymers by dehydration and further carbonization. These formation processes are usually uncontrollable, resulting in the preparation of GQDs with polydispersity.

Top-down



Figure 1: Two main approaches adopted to prepare fluorescent GQDs: the "top-down" splitting route from different carbon sources and "bottom-up" method from small molecules or polymers (reprinted/reproduced with the permission of Ref. [57], copyright 2017, Elsevier B.V.).

2.1 Top-down strategy

2.1.1 Oxidative cleavage

Oxidative cleavage, the most widely used method, is also named oxidation cutting. In this method, the carboncarbon bonds of graphene, GO, or carbon nanotubes are generally broken by H₂SO₄, HNO₃, or other oxidizers. For instance, in the work of Shen et al. [34], GO sheets with a two-dimensional size of micron grade were put in HNO, and cut into the smaller pieces. The products were treated with surface passivation by ethylene glycol and then were reduced by hydrazine hydrate. Eventually, the GQDs with a diameter distribution from 5 to 19 nm were gained. It indicates that blue fluorescence is obtained when the light of a 365-nm wavelength is used to excite the GODs. It is interesting that green fluorescence can be available when the light of a 980-nm wavelength is used. It demonstrates that the as-prepared GQDs have upconversion fluorescence properties. The energy level structural models of GQDs are proposed to explain the process of the formation of fluorescence and upconversion. This work presents a facile method by utilizing hydrazine hydrate to reduce GO with surface passivation for the fabrication of GQDs with frequency upconverted emission. The GQDs may provide a new type of fluorescence and upconversion material for applications in bioscience and energy technology, and may expand the application of graphene-based materials to other fields.

Via et al. [67] presented a simple and controlled method to tune well the lateral size of GO at the nanometer scale. The procedure is shown in Figure 2. First, GO was synthesized from expandable graphite by the modified Hummers method. Then, GO was dispersed into deionized water followed by sonication to obtain a brown GO solution. Later, H_5IO_6 were added into the GO dispersion, and the mixed solution was kept at 60°C for 24 h. The precipitate was centrifuged out from solution and was then washed with deionized water until the supernatant was neutral. After that, sodium polystyrene



Figure 2: Schematic diagram of the synthesis of GQDs for electrochemical detection (reprinted/reproduced with the permission of Ref. [67], copyright 2014, Elsevier B.V.).

sulfonate (PSS) was added into the above GO nanosheet solution and sonicated for 2 h. Finally, l-ascorbic acid (I-AA) was added into the aqueous solution and stirred at 50°C for 24 h. When the reaction ended, the color of the solution turned from yellow to dark black, which was a visual indication that the GO nanosheets were successfully reduced into GQDs with a mixture of different sizes (5-15 nm). The as-prepared GQDs show a strong and excitation-independent PL activity, with the maximum emission wavelength at 470 nm. The excitation-independent emission of the GQDs implies that both the size and the surface state of those sp² clusters contained in GQDs are uniform. In addition, the GQDs show an enhanced performance in the electrochemical sensing of heavy metal ions. A remarkably low detection limit of 7×10^{-9} M for Pb²⁺ is achieved. It is because the GQDs with a high specific surface area can improve the interaction opportunity of active sites and target ions greatly, which endows the capability of accumulating metal ions. The GQDs will be believed to advance the development of not only graphene-based nanosensors but also biomaterial field.

In addition to graphene or GO, other carbon materials, such as fullerenes C60, carbon nanotubes, and carbon fibers, can also be utilized to fabricate GQDs. Fullerene was used as a starting material to produce very small GQDs (2–3 nm) by Pumera et al. [77], due to its well-defined dimension. Treatment of fullerene with a mixture of strong acid and chemical oxidant induced the oxidation, cage-opening, and fragmentation processes of fullerene. The products remained fully dispersed in aqueous suspension and exhibited strong luminescence properties, with the highest intensity at 460 nm under a 340-nm excitation wavelength. Further chemical treatments with hydrazine hydrate and hydroxylamine produced GQDs and resulted in red shift and blue shift of the luminescence, respectively. The present work has demonstrated the simultaneous oxidation and cage opening of fullerene to provide GQDs. The simplicity of this method in producing GQDs shows potential for further development for integration into practical devices or applications including optoelectronics and biological labeling.

The GQDs with fluorescent properties were obtained via oxidation cutting carbon fiber by thick H₂SO₄/HNO₃ under high temperature [31]. The scheme of the procedure is shown in Figure 3A. The as-synthesized GQDs are highly soluble in water and other polar organic solvents, such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). Figure 3B is the transmission electron microscopy (TEM) image of the fiber-derived GQDs, showing relatively a narrow size distribution between 1 and 4 nm, which are summarized in Figure 3B. The high resolution (HR)-TEM image (inset of Figure 3B indicates



Figure 3: Illustration of the preparation process of GQDs by oxidation cutting showing both their morphology and size distribution. (A) Representation scheme of oxidation cutting of CF into GQDs. (B) TEM images of GQDs (synthesized reaction temperature at 120°C); inset of (B) is the HRTEM of GQDs. (C) AFM image of GQDs. (D) Size and height distribution of GQDs (reprinted/reproduced with the permission of Ref. [31], copyright 2012, American Chemical Society).

high crystallinity of the GQDs, with a lattice parameter of 0.242 nm, (1120) lattice fringes of graphene. The atomic force microscopy (AFM) image in Figure 3C demonstrates the topographic morphology of GQDs, the heights of which are between 0.4 and 2 nm, corresponding to one to three graphene layers. The unzipping mechanism consists of the breakup of the fiber structure and the lining up of chemical functional groups (such as epoxy or carbonyl groups) on planar graphitic domains, causing the domains to be prone to fracture, preferably in the zigzag direction. In addition, the research indicates that the size of the GQDs varies with the reaction temperature, and the emission color and the bandgap of GQDs can be controlled accordingly. The as-prepared GQDs show low cytotoxicity and excellent biocompatibility; thus, they can be used as an eco-friendly material in biolabeling and bioimaging.

The GQDs were synthesized using acid treatment and chemical exfoliation of multi-walled carbon nanotubes (MWCNTs) [78]. The as-prepared GQDs have a uniform size distribution, zigzag edge structure, and two-dimensional morphology. It demonstrates that the size of the GQDs is less than 5 nm, and the lattice parameter is estimated to be about 0.25 nm. The results of the research indicate that the GQDs have a bright blue emission upon UV excitation and exhibit high water solubility and good stability. It is shown that the acid treatment of MWCNTs leads to the formation of the functional group in zigzag sites, which results in the pH-dependent fluorescence of the GQDs. This work presents a facile and effective method to obtain GQDs for application in optoelectronics, electronic devices, and biological probes.

Oxidative cleavage or oxidation cutting is simple and effective in the preparation of GQDs, but there are some defects that the strong oxidizer used may cause burning or explosion and the post-processing process is more complicated. Therefore, some new oxidation cutting methods are developed to settle the problems. For instance, Lu et al. [79] utilized black carbon as a precursor and $H_{2}O_{2}$ as a facile oxidant and developed a simple and facile one-pot method for the synthesis of GQDs without using a strong concentrated acid, and the entire synthetic process took only 90 min. In the preparation, black carbon was utilized as a precursor, and H₂O₂ was used as an oxidant to cut the black carbon. The only reaction products were H₂O and GQDs. Thus, the proposed synthetic method not only avoids the use of a strong concentrated acid and the introduction of metal impurity contamination but also does not need any other post-processing steps. The mechanism proposed is that the free radicals (e.g. \cdot OH and \cdot O⁻), which are produced from the decomposition of H₂O₂, have high reactivity and strong oxidizing properties so they can oxidize

and cut the graphene structure of black carbon effectively. The as-synthesized GQDs with diameters ranging from 3.0 to 4.5 nm have robust photo-stability, good resistance to salt solution, low toxicity, and excellent biocompatibility. As a satisfactory FL probe, the GQDs have been successfully applied in FL imaging of HeLa cells directly. Compared with other reported methods, it is the most green and fastest synthesis method for GQDs synthesis to date. The present study provides a green and fast method for the synthesis of GQDs and facilitates GQDs for bioimaging and related biological applications.

2.1.2 Hydrothermal/solvothermal method

The hydrothermal or solvothermal method is a simple and rapid method for the preparation of GQDs. It cut carbon materials into GQDs under the conditions of high temperature and high pressure in the process. Generally, the carbon materials need to be treated through strong oxidation before the reactions happen [42, 80, 81].

The GQDs were prepared from GO as a raw material via the hydrothermal method for the first time by Pan et al. [68]. The procedure is as follows: first of all, GO was mixed in thick H₂SO₄/HNO₂ acid for oxidation, and then, the hydrothermal reaction started under alkaline conditions for about 10 h. Eventually, the GQDs with a size distribution of 5–13 nm were gained. With the reaction mechanism, it was proposed that mixed epoxy chains composed of fewer epoxy groups and more carbonyl groups may exist in the oxidized graphene sheets (GSs), as illustrated in Figure 4A (left). The presence of these linear defects makes the GSs fragile and readily attacked. Some ultrafine pieces surrounded by the mixed epoxy lines and/ or edges may further break up during the hydrothermal deoxidization process, by which the bridging O atoms in the epoxy lines are removed, and thus, the GQDs form eventually (Figure 4A, right). Structural models of GQDs in acidic and alkali media are also proposed based on the reversible protonation of carbene-like zigzag sites and the reversible protonation of oxygen-containing functional groups (Figure 4B). Because the triple carbenes are most common at zigzag edges, the two electronic transitions of 320 nm (3.86 eV) and 257 nm (4.82 eV) observed in the PL spectra can be regarded as transitions from the σ and π orbitals (highest occupied molecular orbitals, HOMOs) to the lowest unoccupied molecular orbital (LUMO), as demonstrated in Figure 4C. The work has developed a hydrothermal method for cutting preoxidized GSs into ultrafine GQDs with strong blue emission. The discovery of the new PL from GQDs may expand the application of



Figure 4: The mechanism for the hydrothermal method and models of the GQDs in acidic and alkali media, as well as typical electronic transitions of triple carbenes at zigzag sites. (A) Mechanism for the hydrothermal cutting of oxidized GSs into GQDs: a mixed epoxy chain composed of epoxy and carbonyl groups (left) is converted into a complete cut (right) under the hydrothermal treatment. B) Models of the GQDs in acidic (right) and alkali (left) media. The two models can be converted reversibly depending on pH. The pairing of $\sigma(\cdot)$ and $\pi(o)$ localized electrons at carbene-like zigzag sites, and the presence of triple bonds at the carbyne-like armchair sites are represented. (C) Typical electronic transitions of triple carbenes at zigzag sites observed in the optical spectra (reprinted/reproduced with the permission of Ref. [68], copyright 2010, Wiley-VCH Verlag GmbH & Co).

graphene-based materials to other fields such as optoelectronics and biological labeling.

Figure 5 presents the hydrothermal strategy for the production of amino-functionalized GQDs (af-GQDs) by Tetsuka et al. [42]. The procedure is as follows: first, homogeneous oxidized graphene sheets (OG) (OG was synthesized according to the modified Hummers method, and all of other agents were obtained from Wako Pure Chemical Industries) water dispersion was mixed with ammonia solution and was heated at 70-150°C for 5 h in an autoclave. After cooling to room temperature, the precipitated insoluble large fragments were filtered out using a 0.02-µm Anopore inorganic membrane (AnodiscTM, Watman). The desired af-GQDs were present in the supernatant. Then, the yellow supernatant was heated and ultrafiltered through centrifugal filter device (Amicon Ultra-4, Millipore). The obtained yellow suspension was further dialyzed through a dialysis tubing membrane



Figure 5: The hydrothermal strategy for the production of amino-functionalized GQDs (af-GQDs) by Tetsuka et al. [42]. (A) Schematic illustration of the preparative strategy for af-GQDs. (B) C1s and N1s X-ray photoelectron spectra for af-GQDs prepared at 90°C (green line) and OGS (gray line). (C) Transmission infrared-absorbance spectra of af-GQDs prepared at 90°C (green line) and OGS (gray line) (reprinted/reproduced with the permission of Ref. [42], copyright 2012, Wiley-VCH Verlag GmbH & Co).

to remove the remaining tiny fragments. As shown in Figure 5A, after being oxidized, the GO starts the hydrothermal reaction in the ammonia system. It is found that the GO is cut into GQDs, and amino substitution reaction happens at the same time. The GQDs with the amino group are gained at last, as proven in Figure 5B and C. The production of uniform af-GQDs with a diameter of ~2.5 nm is verified by TEM. Aqueous suspensions of af-GQDs exhibit bright colorful luminescence under irradiation from a UV lamp with a wavelength of 365 nm. Their corresponding emission peaks vary with the quantity of amine functionalization in the range of 420-535 nm and retain a sharp full width at half maximum (FWHM) as narrow as ~65-80 nm. The research demonstrates a novel strategy for the preparation of GQDs with high efficiency and wide tunability of narrow photoluminescence lines under a single-wavelength UV excitation, whose energy is controlled by their edge-termination structure with primary amines. Their superior optical properties should enable the use of af-GQDs in numerous applications, including multicolor light-emitting devices, biological applications, and photovoltaics.

Significantly, Tian et al. [69] reported a one-step solvothermal method for synthesizing GQDs with the application of hydrogen peroxide in a DMF environment, which introduces no impurity in the whole preparation process. The process is shown clearly in Figure 6. Typically, a muffle furnace was first heated to 800°C for 5 h, and then, 2 g of expandable graphite in an alumina crucible was placed in a high-temperature environment for 10 s to form an expanded graphite. In this step, sulfuric acid and nitric acid molecules decompose into gas and escape from the interlayer of the expanded graphite. The expanded graphite was then mixed with DMF and treated with ultrasound to remove air in the layered structure of the expanded graphite, making full contact between the solvent and the expanded graphite. Subsequently, hydrogen peroxide was added into the mixture and stirred for 5 min to form a homogeneous solution. The final mixture was transferred into an autoclave and heated up to 170°C for 5 h. The product solution was treated with vacuum filtration to obtain GQDs. The mechanism of the reaction is similar to electrochemistry exfoliation of graphite anode: water is oxidized under high redox potential to generate oxygen and hydroxyl radicals, which act as the "scissors" to cut down the graphite anode. It indicates that the diameters of the GQDs were mainly distributed in a range of 20-40 nm, and the thickness mainly falls in the range of 1-1.5 nm, corresponding to two to three graphene layers. As the excitation wavelength increases from 280 nm to 420 nm, the PL intensity increases to maximum and then decreases, while the PL peaks shift from 398 nm to 480 nm. The quantum yields of 15% in neutral conditions and good photoluminescence stability in different pH conditions are demonstrated, implying a wider application in different harsh environments. This



Figure 6: Schematic representation of GQDs prepared by solvothermal method (reprinted/reproduced with the permission of Ref. [69], copyright 2016, Elsevier B.V.).

is the first time that GQDs were prepared from graphite materials by hydrogen peroxide without a dialysis process. Because of the extremely low cost, good water solubility, high quantum yield, no need for dialysis for purification, and easily-obtained experiment equipment, this method shows great promise in the biomedical field and electronic device.

It is noteworthy that Liu et al. [82] reported a facile one-pot synthesis method using graphite as the starting material, which can selectively obtain either pure GO or pure GQDs within 2 h, with a higher production yield (93% for GO and 10% for GQDs). The synthesis process is elaborated in Figure 7, that is, graphite powder is mixed with potassium permanganate, and sulfuric acid is gradually added under magnetic stirring. Then, nitric acid is introduced into the autoclave, which is heated to a certain temperature for the desired products. It proves that the size (from 50 to 2.5 nm) of the GQDs can be

tuned by simply varying the ratio of graphite and potassium permanganate. The emission spectra of the 2.5-nm GOQDs demonstrate a perfect excitation-dependent photoluminescence behavior. The strong luminescence emission suggests a high luminescence yield (about 8.8%) and, sequentially, a high quality of the as-synthesized GOQDs. It should be mentioned that typical solvothermal methods, utilizing graphene oxide as a precursor, need more complicated processing when compared with this strategy. This one-pot synthesis method has the following unique characteristics: (1) the operation procedure is simplified because the reaction happens in a sealed autoclave; (2) GO or GQDs can be selectively obtained by simply adjusting the reaction temperatures; (3) the size of the GQDs can be easily tuned from 50 to 25, 13, 5, and finally to 2.5 nm, with strong luminescence emission; (4) various carbon sources, including MWCNTs, singlewalled carbon nanotubes (SWCNTs), carbon black, etc.,



Figure 7: Schematic representation of the solvothermal reaction route, which involves exfoliating graphite to GO and further cutting of GO layers to GOQDs at given experimental conditions (reprinted/reproduced with the permission of Ref. [82], copyright 2017, Wiley-VCH Verlag GmbH & Co).

can all be utilized for the fabrication; (5) this method also allows large-scale synthesis of both pure GO and pure GQDs.

2.1.3 Microwave-assisted/ultrasonic-assisted process

As we know, one of the common problems is the long reaction time when the oxidative cleavage or hydrothermal/ solvothermal method is used. The microwave technique, as a rapid heating method, is widely used for the preparation of nanomaterials. It not only can shorten the reaction time but also improve the production yield. Accordingly, electrochemiluminescent (ECL) two-color GQDs were fabricated by the cleavage of GO in the acidic condition via the microwave-assisted method by Li et al. [38]. The oxidation reaction was shortened, and the yield was improved to around 8%. Figure 8 outlines the preparation route to greenish-yellow luminescent GQDs (gGQDs, unreduced) and bright blue luminescent GQDs (bGQDs, further reduced with NaBH₄). For the preparation of stabilizer-free gGQDs, GO nanosheets were kept under acid conditions (3.2 M HNO, and 0.9 M H₂SO₄) within 3 h. Then, bGQDs were obtained via moderately reducing gGQDs with NaBH, within 2 h. It indicates that the diameters of gGQDs are mainly distributed in the range of 2–7 nm with

an average diameter of 4.5 nm, and the dimensions and height of the bGQDs show no perceptible change, demonstrating that the PL blue shift of the bGQDs is attributed to their structural change after reduction rather than their dimension variation. The PL quantum yields of gGQDs and bGQDs are as high as 11.7% and 22.9%, respectively. Briefly, the cleaving mechanism is described as follows: initiated by the acid oxidation of epoxy groups, it is prone to form a mixed line on the carbon lattice composed of fewer epoxy groups and more carbonyl groups, making the graphitic domains fragile and readily attacked. This kind of ECL-active GQDs are expected to have promising applications in the development of novel ECL biosensors due to their low cytotoxicity, low cost, excellent solubility, and ease of labeling.

The GQDs were synthesized by the microwaveassisted pyrolysis method using the following procedure by Zhang et al. [70]. In the preparation, aspartic acid (Asp) and NH₄HCO₃ were added to 20 ml of deionized water in a beaker and then were heated using microwave irradiation for 10 min. The products were further purified by dialyzing against deionized water using a membrane with a dialysis membrane for 7 h to obtain the final GQDs. The diameters of the GQDs are mainly distributed in the narrow range of 1.8–2.4 nm with an average size of 2.1 nm. The solution of the GQDs emits bright blue luminescence under the



Figure 8: Schematic representation of the preparation route for gGQDs and bGQDs (reprinted/reproduced with the permission of Ref. [38], copyright 2012, Wiley-VCH Verlag GmbH & Co).

irradiation of UV light (365 nm). The as-synthesized GQDs possess lower cellular toxicity and high photostability, and is very sensitive not only to the pH value but also to iron ions. Therefore, the GQDs can serve as a fluorescent probe for the sensitive detection of Fe^{3+} and pH value and can be directly used for live cell imaging.

Besides, the ultrasonic technique is also a commonly used method in the synthesis of materials. Tens of thousands of small bubbles in the liquid will form in the presence of ultrasonic waves and produce instantaneous high pressure and high energy when growing, shrinking, and collapsing, destroying the carbon-carbon bonds. For instance, an environmental friendly, fast, and industrial promising method for synthesizing GQDs at a large scale was reported via an ultrasonic-assisted liquidphase exfoliation technique [71]. The GQDs with different sizes, structures, and defect contents were obtained using different graphitic carbon precursors for exfoliation, and the production yield of GQDs can reach 3.8 mg/ ml. In a typical preparation of GQDs, acetylene black was dispersed in N-methyl-2-pyrrolidone (NMP) solvent. The dispersion was then under mild ultrasonication for 1 h. A gray liquid containing dispersed GQDs and some residual precipitates was obtained. The precipitates were removed by centrifugation at 10,000 rpm for 30 min, obtaining a homogeneous gray dispersion of GQDs. It shows that the size distribution of GQDs is between 2 and 6 nm, and the thickness distribution is of 0.4–2 nm, indicating a monolayer to a few layers of GQDs. The GQDs exhibit strong excitation-dependent PL behavior. When excited at the wavelength range from 310 to 490 nm, the PL shows red shifts from 428 to 528 nm. The present work offers a new strategy for large-scale synthesis of GQDs with different contents of defects and edge structures, which can be used as the initials for further functionalization in the application of biology, electronic, energy, and engineering.

For the first time, an integrated $O_3/H_2O_2/ultrasound$ process was proposed for the innovative synthesis of GQDs by Wen et al. [83]. Typically, a GO aqueous suspension was mixed with H_2O_2 in a quartz tube, continuously purged with O_3 for 3 h under ultrasonic condition. Then, the nitrogen was bubbled into the resulting suspension for 15 min to terminate the reaction. The solid GQDs can be obtained via vacuum freeze drying. The resultant GQDs exhibit excellent PL performances with uniform lateral dimensions of 4–10 nm. It indicates that the PL intensities become stronger as more GO fragments are further cut into undersized pieces with the prolonging of $O_3/H_2O_2/ultra$ sound treating time. The possible synthesis mechanism isproposed in Figure 9. The reaction process mainly consists

of two steps. In the first stage, the C=C/C-C bands near the defects and sp³ carbons in GO are more prone to be oxidized and cut down by the generated ·OH assisted by ultrasound. The ultrasound is supposed to increase the amount of •OH and also strengthen the molecular vibration, thus, speeding up the GO breakage into undersized fragments. Meanwhile, the oxidation of •OH leads to an obvious increase in the total oxygen-containing groups upon the GO surface. With the prolonging of the reaction time, the generated ·OH radicals accumulate and cause further cleavage and oxidization of the GO fragments under the promotion of ultrasound, leading to the generation of the GQDs. This study put forward a facile and efficient synthesis route of high-purity -COOH-enriched GQDs, and it is based on the synergetic oxidative tailoring of GO into quantum dots by the O₂/H₂O₂/ultrasound process. Moreover, it is expected to advance the fundamental research of quantum dots and the applications of the as-generated GQDs in other potential fields such as solar cell, fluorescent detection, cellular imaging, and so on.

Interestingly, a novel method that combined the merits of microwave-assisted and ultrasonic-assisted processes was reported by Luo [84]. In the work, whitelight-emitting GQDs (WGQDs) were prepared by a facile two-step microwave-assisted hydrothermal method (as shown in Figure 10). The procedure is as follows: yellow-green fluorescent GQDs are synthesized beforehand through exfoliation of oxidized graphite under the ultrasonication and microwave irradiation. The GQDs show their average lateral size of 2.5 nm, and the average height of the GQDs is calculated to be about 2 nm from the AFM height image. After further reaction under microwave irradiation in alkaline solution (pH 13.0), the GQDs were converted to WGQDs with photochemical stability and nontoxicity. As shown from the TEM images, the lateral size of the WGQDs is still kept at about 2-5 nm. The AFM height image of the WGQDs evaluates that the height of the WGQDs is about 1.25-2.75 nm, indicating that the as-prepared WGQDs consisted of multilayer (two to five layer) graphene. The crystal lattice spacing of 0.335 nm can be clearly observed in the HRTEM image. When the colloidal solution of the WGQDs is excited at 365 nm, the PL spectrum exhibits a broad emission band at 445 nm along with a relatively weak peak at 575 nm. It can be observed that the fluorescent intensity of the WGQDs decreases with the change in the excitation wavelength from 325 to 400 nm. The WGQDs are subsequently used as a phosphor to fabricate a white-light-emitting diode (WLED) device by a solution-processing method. The WLED based on the WGQDs clearly displays better the white electroluminescence performance than that of the



Figure 9: Schematic illustration of the possible two-step generation mechanism of GQDs (reprinted/reproduced with the permission of Ref. [83], copyright 2016, Elsevier B.V.).



Figure 10: Schematic presentation of preparing WGQDs. (reprinted/reproduced with the permission of Ref. [84], copyright 2016, Wiley-VCH Verlag GmbH & Co).

previously reported WLED based on the GQDs or carbon dots. Therefore, this study presents a novel method and demonstrates that WGQDs used as a single-phase whitelight-emitting phosphor are expected to be a highly efficient avenue to improve the performance of WLED based on carbon nanomaterials.

2.1.4 Electrochemical oxidation

In the electrochemical oxidation method, graphite, graphene, or carbon nanotubes work as a working electrode and are oxidatively cleaved into the GQDs under high REDOX voltage ($\pm 1.5 \sim \pm 3$ V). There are two approaches

for the electrochemical oxidation. One is that the carbon-carbon bonds of graphene or carbon nanotubes are directly fractured by electrochemical oxidation. The other is that water is oxidized to turn into a hydroxyl free radical (\cdot OH) or an oxygen free radical (0·), which can oxidatively cleave them into GQDs. The GQD solutions gained by the electrochemical oxidation method show high levels of stability, but their disadvantage is that both the pretreatment of raw materials and the purification of GQDs products take a long time. Moreover, it is difficult to realize the mass production of the GQDs because of the low product yield.

In the study of Li et al. [72], the graphene filter film was used as a working electrode, and the phosphate buffer solution (PBS) was utilized as the electrolyte to fabricate GQDs. The electrochemical preparation of functional GQDs was performed by the CV scan within ± 3.0 V at a scan rate of 0.5 V s⁻¹ in 0.1 M PBS. The graphene film (5 mm × 10 mm) was used as a working electrode. Pt wire and Ag/AgCl were used as counter and reference electrodes, respectively. Graphene film was prepared by filtration and treated with O₂ plasma for seconds prior to the preparation of the GQDs were collected after filtering and dialyzed with a cellulose ester membrane bag. The asprepared GQDs have a uniform size distribution (3–5 nm), present a green luminescence, and can be retained stably

in water for several months without any changes. Next, the research group replaced PBS with acetonitrile containing tetrabutylammonium perchlorate, as the electrolyte, and made the nitrogen-doped GQDs (N-GQDs) with a size of 2–5 nm [45]. Unlike their N-free counterparts, the newly produced N-GQDs with an N/C atomic ratio of ca. 4.3% emit blue luminescence and possess an electrocatalytic activity comparable to that of a commercially available Pt/C catalyst for the oxygen reduction reaction (ORR) in an alkaline medium. In addition to their use as metalfree ORR catalysts in fuel cells, the superior luminescence characteristic of N-GQDs allows them to be used for biomedical imaging and other optoelectronic applications.

Similarly, Shinde et al. [73] utilized propylene carbonate containing LiClO_4 as the electrolyte and prepared GQDs by cutting MWCNTs via a two-step electrochemical oxidation. The sizes of the GQDs can be regulated by changing the temperature and electrolytic time. Figure 11 represents the two-step process for the electrochemical transformation of the MWCNTs to GQDs. The first step comprises the application of a typical anodic potential of 1 V vs. Pt QRE (quasi reference electrode) to the MWCNT-coated working electrode in propylene carbonate with LiClO_4 , in which the applied electric field initiates the breaking of sp² carbon atoms. More interesting is the variation with respect to the time of oxidation and also changes in the second step after applying a potential of -1 V vs. QRE. This is attributed to



Figure 11: Schematic representation of various processing stages involved in the preparation of photoluminescent GQDs from MWCNTs by this electrochemical approach (reprinted/reproduced with the permission of Ref. [73], copyright 2012, Wiley-VCH Verlag GmbH & Co).

the intercalation of Li⁺/propylene carbonate complexes resulting in exfoliation of oxidized MWCNTs, facilitating the formation of size-tunable GQDs. This work has presented a new electrochemical approach to size-tunable GQDs [$3(\pm 0.3)$, $5(\pm 0.3)$, $8.2(\pm 0.3)$ nm at 90°C, $23(\pm 2)$ nm at room temperature] from MWCNTs in a non-aqueous solution without using any molecular capping agent for the first time. These GQDs are especially useful for cellular and molecular imaging applications due to intrinsic luminescence behavior, higher photostability, and enhanced fluorescence quantum yield.

2.1.5 Other methods

Because of the unique structure and excellent properties of GQDs, more and more preparation methods have been reported, such as the chemical vapor deposition (CVD) [85–87], pulsed laser ablation (PLA) [88–91], and electron-beam irradiation [92]. For instance, Lee et al. [93] reported the size-controlled fabrication of uniform GQDs using self-assembled polystyrene-b-polydimethylsiloxane (PS-PDMS) block copolymers (BCPs) as an etch mask on graphene films grown by chemical vapor deposition (CVD). Figure 12 illustrates the chemical structure of the BCP and a schematic of the overall process to obtain GQDs on an SiO₂/Si substrate. The first step of the fabrication process is the self-assembly of a PS-PDMS BCP film on a graphene/Si/SiO₂ substrate. The single-layer graphene on the Si/SiO, substrate was prepared using CVD and then treated with a thin (3-4 nm) hydroxyterminated PDMS homopolymer brush. The PS-PDMS BCP was dissolved in toluene and spin-coated onto the substrate. In the second step, oxygen plasma etching processes produced well-ordered silica dot arrays with hexagonal symmetry, which were used as a masking layer for the patterning of the GQDs (Figure 12B). Although adjacent silica dots were very closely packed, GQDs were overetched depending on the condition of the oxygen plasma treatment. Electron microscope images show that the as-prepared GQDs are composed of mono- or bilayer graphene with diameters of 10 nm and 20 nm, corresponding to the size of BCP nanospheres. In the measured PL spectra, the emission peak of the GQDs on the SiO₂ substrate is shown to be at ~395 nm. This research provides a noteworthy contribution to enhancing the properties of GQDs and to the understanding of the effects of size and functionalization on GQDs.

Significantly, a facile and remarkably rapid method for production of GQDs exhibiting excellent optoelectronic properties was reported by Kang et al. [88]. In this work, the pulsed laser ablation technique (PLA) is employed to exfoliate GQDs from MWCNTs. The procedure is as follows: MWCNTs were dispersed in n-hexane and



Figure 12: The chemical structure of the BCP and a schematic of the overall process to obtain GQDs on an SiO_2/Si substrate. (A) Chemical structure of the BCP. (B) Schematic illustration of the fabrication of GQDs including the spin coating of BCP, formation of silica dots, and etching process by O_2 plasma (reprinted/reproduced with the permission of Ref. [93], copyright 2012, American Chemical Society).

ethanol mediums, respectively. Ultrasonication was subsequently performed on the solutions for 2 h in order to achieve homogeneous dispersion of MWCNTs. Fifty milliliters of the solution were transferred into glass vials, and then the PLE process was performed on the fixed vials for 6 min using a Quanta Ray-LAB 190 equipment (Spectra-Physics, USA). The laser was focused on the center of the vials with a focal length of 10 cm and a spot diameter of 10 mm² to prepare the GQDs. Strikingly, it takes only 6 min to transform all the MWCNT precursors to GODs. Further-

10 mm² to prepare the GQDs. Strikingly, it takes only 6 min to transform all the MWCNT precursors to GQDs. Furthermore, it can control the oxidation degree of the GQDs by simply changing the organic solvents utilized in the processing. The as-prepared GQDs show a distinct blue PL with excellent quantum yield (QY) up to 12% as well as sufficient brightness and resolution suitable for optoelectronic applications. This work will further open up new routes for the preparation of different optoelectronic nanomaterials.

Moreover, in the study of Wang et al. [92], a room temperature strategy for the synthesis of single-crystalline fluorescent GQDs via electron beam irradiation was reported. The precursor containing high-activity nitro groups is easy to fusion GQDs with the method. Under optimized conditions, the GQDs exhibit highly efficient fluorescence at 475 nm with a quantum yield of 32%. The PL maximum corresponds well with the excitation wavelength. In addition, the single-exponential fluorescence lifetime (4.86 ns) exhibits the intrinsic PL characteristic. The pH stability in neutral and alkaline solution, solid solubility, and storage time stability of GQDs are satisfactory. It is demonstrated that the GQDs can be applied as a safety fluorescent probe for cell imaging.

Besides, GQDs were fabricated through grinding of graphite in ionic liquid by Papakonstantinou et al. [94]. The size distribution of the GQDs was wide (from 2 to 29 nm), and the thickness was of two to five atomic layers. The advantage of this method is that there is no introduction of oxygen-containing functional groups on the GQDs, but the thickness of the GQDs is difficult to control, and normally, multilayer GQDs are gained. Kim et al. used oxygen plasma to cut graphene into the GQD array with templates of block copolymer. The size of the GQDs and the array pitch can be adjusted by template morphology [95]. Lin et al. inserted potassium atoms into the layers of MWCNTs, forming an intercalation compound and then cleaved the MWCNTs into GQDs under the energy that was generated by violent reaction of potassium atoms with water [55]. Kotchey et al. [96] fabricated GQDs from GO with enzyme catalytic oxidation, with the reaction time lasting for dozens of days. GQDs were made through the extension of oxidation time

(4–5 days) via the Hummers method by Zhang et al. [97]. Small amounts of GQDs were gained using a ruthenium catalyst for the catalytic cracking of fullerene by Lu et al. [98]. GQDs were gained through separating different sizes of GO via density gradient centrifugation by Sun et al. [99]. The GQDs were isolated from GO via selective precipitation by Shi et al. [100]. However, these methods have defects of low yield, long reaction time, or complicated process and are not popularly used.

2.2 Bottom-up strategy

2.2.1 Controllable synthesis

In this method, GQDs are synthesized from phenyl-containing compounds through stepwise controllable synthesis in the organic solvent. The as-synthesized GQDs have an accurate number of carbon atoms, uniform size, and shape. However, the preparation process includes multistep complicated chemical reactions, which are not only consumed for a long time but are also of low yield. For instance, GQDs containing 168, 132, and 170 carbon atoms (denoted by 1, 2, 3, respectively, as shown in Figure 13A) were fabricated via this method by Li et al. [74]. The 2',4',6'-trialkyl phenyl molecules (TPM) were connected to the edge of the GQDs in order to prevent the GQDs from reuniting. The possibility of the GQDs overlapping with each other was reduced, and the dispersibility in the organic phase was improved, because of the steric hindrance caused by TPM stretching in three-dimensional direction. The synthesis of 1-3 is outlined in Figure 13B. It starts from small-molecule precursors, such as 3-iodo-4-bromoaniline (denoted by 4) and other substituted benzene derivatives, to synthesize two key intermediates (denoted by 5 and 6, respectively). Subsequently, stepwise Suzuki coupling reactions lead to polyphenylene dendritic precursors for 1-3, which are then exposed to an excess of FeCl, in a dichloromethane/nitromethane mixture, yielding the graphene quantum dots. The quantum dots 1 and 3 presented here, in particular, have large extinction coefficients in a wide spectral range from UV to near-infrared and, thus, can serve as a new type of light-harvesting media for photovoltaics. This work demonstrates the versatile synthesis of large, stable colloidal graphene quantum dots with desired sizes and structures enabled by a new solubilization strategy.

Sulfur-doped GQDs (S-GQDs) with bright blue emission have been prepared from 3-mercaptopropionic acid (MPA) and 1,3,6-trinitropyrene (TNP) by a facile one-pot



Figure 13: The synthesis process of graphene quantum dots and their molecular structures. (A) Structure of graphene quantum dots 1–3. (B) Synthesis of graphene quantum dots 1–3 (reprinted/reproduced with the permission of Ref. [74], copyright 2010, American Chemical Society).



Figure 14: Schematic illustration for the preparation of blue S-GQDs and turn-off detection of Ag⁺ (reprinted/reproduced with the permission of Ref. [101], copyright 2017, Elsevier B.V.).

method [101]. Briefly, MPA and TNP were first mixed by ultrasonic and placed into an autoclave for hydrothermal treatment at 200°C for 10 h. Then, the solution containing water-soluble GQDs was filtered through microporous membrane to remove the insoluble carbon product, and un-reacted small molecules were removed by dialyzing. After dialysis, a pale-yellow aqueous suspension of the S-GQDs was obtained and freeze dried. The possible structure of S-GQDs is given in Figure 14. The -SH groups of MPA add to the pyrene ring in the hydrothermal reaction. The carboxyl groups in the MPA link to the GQDs at the same time to exhibit the -COOH modification. Also, some S atoms may be captured and fused in the graphene lattice. The synergistic effect of S-doping and -COOH in the GQDs may possess special coordination abilities and corresponding selectivity toward metal ions. The S-GQDs are successfully explored as a sensing probe for Ag⁺ detection with high sensitivity and selectivity. The ease of the one-step synthesis and the promising performance of the S-GQDs make this work attractive in bioimaging, sensing, optoelectronic devices, and catalysis.

2.2.2 Carbonization

The molecular carbonization is an environmentally friendly and facile method, which utilizes suitable organic molecules or polymers for dehydration and further carbonization [49, 57, 75, 102]. The GQDs with polydispersity are obtained because the size and the structure are difficult to be controlled precisely for this method. For

instance, low-cost and high-yield green-photoluminescent single-layer GQDs were synthesized with only deionized water and glucose as a precursor via this method [102]. In a typical synthesis, glucose powder was dissolved in deionized water. The mixture was treated in an autoclave at 200°C for 8 h. The initial liquid sample was transparent (colorless), and it changed to orange after the synthesis of SLGQDs. The mechanism is presented as follows: under the hydrothermal process, glucose molecules are dehydrated to form C=C, which is the elementary unit of the graphene structure. During the formation of the QDs, the hydrogen atoms of a glucose molecule interact with the hydroxyl groups of an adjacent glucose molecule leading to the formation of water molecules. Consequently, carbon atoms covalently interact with each other, and finally, GQDs are formed, as schematically shown in Figure 15. The SLGQDs have a uniform dispersion without any apparent aggregation with an average size of about 8 nm. When the SLGQD solution is excited at wavelengths from 450 to 520 nm with an interval of 10 nm, the emission peaks of the sample at various excitation wavelengths do not shift, and the maximum emission wavelength remains at around 540 nm. It implies that both the size and the surface state remain uniform, and the product is green photoluminescent. This facile method is presented to prepare the SLGQDs from only glucose powder as a precursor in DI water, and shows the prominent advantages of low-cost, high-yield, and large-scale production over the reported ones.

A simple carbonization method for the preparation of both GQDs and GO has been developed by tuning the



Figure 15: Formation mechanism of the SLGQDs via a hydrothermal method at 200°C for 8 h (reprinted/reproduced with the permission of Ref. [102], copyright 2017, Elsevier B.V.).



Figure 16: Diagram for the synthesis of GQDs and GO. The black dots in the GO represent oxygen atoms (reprinted/reproduced with the permission of Ref. [75], copyright 2012, Elsevier B.V.).

carbonization degree of citric acid (CA) and dispersing the carbonized products into alkaline solutions [75]. The preparation schematic of the GQDs and GO is shown in Figure 16. In a typical procedure of the GQD preparation, 2 g of CA was put into a 5-ml beaker and heated to 200°C using a heating mantle. About 5 min later, the CA was liquated. Subsequently, the color of the liquid was changed from colorless to pale yellow, and then orange in 30 min, implying the formation of the GQDs. If the heating was kept on, the orange liquid would finally turn to black solid in about 2 h, suggesting the formation of GO. The as-prepared GQDs are ~15 nm in width and 0.5-2.0 nm in thickness. They show a relatively strong (9.0%) PL quantum yield and an excitation-independent PL emission activity. In contrast, the GO nanostructures consist of sheets that are hundreds of nanometers in width and ~1 nm in height, exhibiting a relatively weak (2.2%) PL quantum yield. This work presents a simple bottom-up method to selectively prepare GQDs and GO by tuning the carbonization degree of a common organic precursor CA. Additionally, Naik et al. [103] have reported the pyrolysis of CA and further addition of sodium hydroxide for maintaining the PH for fabrication of GQDs. The CA decomposes and the

hydronium ion formed from the acid acts as a catalyst in the subsequent decomposition reaction. Aromatization and formation of aromatic clusters take place via aldol condensation and cycloaddition, after further addition of sodium hydroxide. Eventually, GQDs are produced at a different pH. In this work, the pH plays an important role in the formation of GQDs from citric acid.

Besides, there are some reports that biomass or polymers are also utilized to fabricate GQDs by this method. In the work of Teymourinia et al. [104], the GQDs were prepared from corn powder as a green precursor. In typical synthesis, corn powder was dispersed into DI water and stirred, and then the solution was transferred into a Teflon-lined stainless autoclave and heated at 180°C for 8 h. At last, the solution was centrifuged at 14,000 for 15 min to separate the GQDs, which were uniform in size ranging from 20 to 30 nm in diameter. A broad emission centered at 450 nm is observed in the emission spectrum (PL) with an excitation wavelength at 360 nm and the excitation spectrum (PLE) revealing a broad peak centered at 365 nm. This work presents novel and green methods to synthesize GQDs using corn powder. Rice husk biomass was also utilized as an abundant source to controllably prepare

	Methods	Advantages	Disadvantages
Top-down strategy	Oxidative cleavage	It is the most widely used method, which can achieve to mass production because it is simple and effective	Some strong oxidizer, which need to be used may cause burning or explosion, and the post- processing process is complicated
	Hydrothermal/ solvothermal method	It is a simple and rapid method Additionally, hydrothermal method is environmentally friendly	The carbon materials need to be treated through strong oxidation before the reactions happen
	Microwave-assisted/ ultrasonic-assisted process	It not only can shorten the reaction time, but also can improve the production yield	Microwave/ultrasonic reactor is expensive, and the volume is limited in industrial production
	Electrochemical oxidation	The GQDs obtained by this method show high levels of stability, and the size distribution is uniform	Pretreatment of raw materials and the purification of GQD products take a long time. Moreover, it is difficult to realize the mass production because of the low product yield
Bottom-up strategy	Controllable synthesis	The as-prepared GQDs have accurate number of carbon atoms, uniform size and shape	The preparation process includes multistep complicated chemical reactions, which not only consume long time but also are of low yield
	Carbonization	It is an environmentally friendly and facile method	GQDs with polydispersity are obtained because the size and structure are difficult to be controlled precisely

Table 1: The respective advantages and disadvantages of different methods.

high-quality GQDs with a yield of 15 wt% [105]. The asfabricated GQDs can be stably dispersed in water, exhibiting bright and tunable photoluminescence. It is worth noting that mesoporous silica nanoparticles are also synthesized as a byproduct during the fabrication of GQDs. This strategy achieves a comprehensive utilization of rice husks, exhibiting tremendous benefits on both economy and environment. Zhou et al. [76] presented a simple and effective approach toward PL GQDs using commercially available polycyclic aromatic hydrocarbon (PAHs) as the precursors. The obtained PL GQDs have sizes of 5-10 nm and thicknesses of 0.5-2 nm, exhibiting excellent water solubility, low toxicity, high optical stability, and tunable fluorescence. It was shown that the PL GQDs could be used as fluorescent probes for highly sensitive Fe³⁺ and H₂O₂ detection. The present work paves the way for scalable and low-cost synthesis of PL GQDs, which will enable further exploration of their applications in the biomedical and optoelectronic fields.

In general, the top-down strategy is extensively used in the preparation of GQDs. The GQDs are gained from carbon materials, including graphene, fullerenes, carbon nanotubes, etc., by cutting them via chemical or physical methods, such as oxidative cleavage, hydrothermal or solvothermal method, electrochemical oxidation, ultrasonic-assisted or microwave-assisted process, and laser ablation. For the bottom-up strategy, the GQDs are fabricated through controllable synthesis or carbonization from suitable organic molecule or polymers. The respective advantages and disadvantages of the different methods are summarized in Table 1.

3 Potential applications

3.1 Sensors

The interaction between GQDs and certain substances can cause fluorescent intensity of the GQDs to be reduced. According to this principle, a variety of chemical or biological sensors can be designed to detect heavy metal ions [106, 107], small organic or inorganic molecules [108, 109], biological molecules [110, 111], etc. For instance, Wang et al. [112] made use of GQDs to detect Fe³⁺ ions. It is found that Fe³⁺ ions have a significant impact on the fluorescence intensity of GQDs because of the special complexation between Fe³⁺ ions and the phenolic hydroxyl groups of the GQDs. When the concentration of Fe³⁺ ions in the solution arrive to 80 ppm, the fluorescence of GQDs is quenched. However, other metal ions with the same concentration have little impact on the fluorescence intensity. It shows that the GQD-based sensors to Fe³⁺ ions are highly selective. Fan et al. [108] investigated using GODs to detect trinitrotoluene (TNT) in solution, based on the fluorescent quenching of GQDs by TNT. It demonstrates that TNT is adsorbed on the surface of the GQDs by a π - π interaction, and fluorescence resonance energy transfer is caused by molecular dipole-dipole interaction within a certain distance, reducing the fluorescence intensity of GQDs. Li et al. [38] designed a new type of electrochemical fluorescent sensors to test Cd²⁺ ions, taking advantage of the electrochemical fluorescence emission properties of the GQDs.

Moreover, GQDs have excellent electrical conduction ability, good dispersibility, and a large specific surface area, and is advantageous for the biological molecules to load on its surface. Therefore, Shehabab et al. [110] utilized a simple route to prepare GQDs via glucose carbonization for a nonenzymatic glucose sensor. GQDs functionalized with phenylboronic acid (PBA) receptors were employed as a sensing material. The developed sensor has a linear response to glucose over a concentration range of 4-40 mM with a correlation coefficient of 0.97 and a low detection limit of approximately 3.0 mm. The fluorescence enhancement after the addition of PBA is caused by the coupled effect between the conjugated aromatic rings of the GQDs and PBA functional groups, as indicated in the schematic diagram of Figure 17. Maleimide-functionalized GQDs (M-GQDs) were synthesized and deployed for biothiol (cysteine, homocysteine, or glutathione) recognition following the principle of Michael addition [111]. The M-GQDs probe is found to be highly sensitive and selective toward biothiol detection in the nanomolar range in

aqueous solution and at a physiological pH (7.0). Moreover, a fluorescence immunoassay sensor was fabricated to detect immunoglobulin G (Ig G), based on the fluorescence resonance energy transfer mechanism [113]. In the work of Liu et al. [43], highly photoluminescent glycine (GLY)-functionalized GQDs (GLY-GQDs) were synthesized by a simple and green pyrolysis method employing ethylene glycol as the carbon source. The as-synthesized GLY-GQDs exhibit excellent water solubility with a fluorescence quantum yield of 21.7%. GLY-GQDs can be used as the fluorescence probe of ascorbic acid (AA), based on the quenching effect of Ce(IV) to GLY-GQDs and the special redox reaction between AA and Ce(IV), as shown in Figure 18.

Besides, Zhang et al. [114] fabricated a nanofibrous membrane of GQDs by electrospinning water-soluble GQDs with polyvinyl alcohol (PVA) directly. For the first time, the created PVA/GQD nanofibrous membrane was utilized to fabricate dual-purpose fluorescent and electrochemical biosensors for the highly sensitive determination of hydrogen peroxide (H_2O_2) and glucose. The experimental results indicated that the fluorescence intensity of the nanofibrous membrane decreased linearly with increasing H_2O_2 concentration because the addition of H_2O_2 leads to fluorescence quenching of the GQDs. After binding glucose oxidase onto the created nanofibrous membrane,



Figure 17: Representation scheme of the proposed enhancement and quenching mechanism of GQDs fluorescence (reprinted/reproduced with the permission of Ref. [110], copyright 2017, Elsevier B.V.).



Figure 18: "Off-on" fluorescence system of GLY-GQDs-Ce⁴⁺-AA (reprinted/reproduced with the permission of Ref. [43], copyright 2017, Elsevier B.V.).

the fabricated nanofibrous membrane showed high sensitivity and selectivity for glucose detection. In addition, the PVA/GQD nanofibrous membrane can also be directly electrospun onto an electrode for the electrochemical detection of H_2O_2 . This novel nanofibrous membrane exhibits excellent catalytic performance and fluorescence activity and, therefore, has potential applications for the highly stable, sensitive, and selective detection of H_2O_2 and glucose.

In the work of Lin et al. [115], photoluminescent GQDs (2-5 nm) have been used for the first time as moleculelike building blocks to construct self-assembled hybrid materials for label-free biosensors. Ionic self-assembly of disc-shaped GQDs and charged biopolymers is found to generate a series of hierarchical structures that exhibit aggregation-induced fluorescence quenching of the GQDs and change the protein/polypeptide secondary structure. The integration of GQDs and biopolymers via self-assembly offers a flexible toolkit for the design of label-free biosensors in which the GQDs serve as fluorescent probes, and the biopolymers provide a biological function. This work indicates that the integrative self-assembly of biomolecules and GQDs will open up new avenues for the design of multifunctional biomaterials with combined optoelectronic properties and biological applications.

The design of a novel functional peptide molecule was reported by Li et al. [116], which has the abilities to form peptide nanofibers (PNFs) and recognize with GQDs and GO nanosheet specifically. Based on the design of peptide sequence, the ternary GQD-PNF-GO nanohybrids are successfully synthesized. It is found that the GQD-PNF-GO nanohybrids show potential applications for high performance electrochemical hydrogen peroxide (H_2O_2) biosensor. This fabricated biosensor exhibits high sensitivity and selectivity, low detection limit, and wide linear range for sensing H_2O_2 . The strategies shown in this work will benefit the further creation of functional binary and ternary nanomaterials, as well as the understanding of their self-assembly and formation mechanisms.

Significantly, Ju et al. [117] synthesized highly blueluminescent nitrogen-doped graphene quantum dots (N-GQDs) by a facile one-step hydrothermal treatment of citric acid and dicyandiamide. A quantum yield (QY) as high as 32.4% is achieved at an excitation wavelength of 350 nm. It is found that such N-GQDs with a high QY can be used as efficient fluorescent probes for the detection of glutathione (GSH). In the detection, the photoluminescence (PL) intensity of the N-GQDs could be quenched by mercuric ions due to the strong electrostatic interaction and electron transfer between N-GQDs and Hg(II). Upon the addition of GSH, the PL intensity of N-GQDs can be recovered owing to the preferred combination of Hg(II) and GSH by forming a Hg(II)-S bond. Under optimal conditions, this fluorescence turn-on sensing system exhibits excellent sensitivity and selectivity for GSH determination with a detection limit of 87 nM. Importantly, the N-GQDs-Hg(II) system can be successfully applied for visualizing the intracellular GSH in live HeLa cells due to bright luminescence, low cytotoxicity, and good biocompatibility. Furthermore, they designed a novel colorimetric sensor for more sensitive detection of GSH based on the intrinsic peroxidase-like activity of Ag nanoparticles supported on the nitrogen-doped graphene quantum dots (Ag NPs-N-GQDs) [118]. The Ag NPs-N-GQDs nanocomposites can catalyze the oxidation of 3,3'5,5'-tetramethylbenzidine (TMB) to oxTMB with the presence of H₂O₂ along with a visual color variation. As GSH can reduce oxTMB, the UV-vis absorption intensity of oxTMB shows a strong dependence on the concentration of GSH. The novel Ag NPs-N-GQDs-TMB-H₂O₂ system exhibits more high sensitivity and selectivity for the detection of GSH with a lower detection limit of 31 nM and a wide detection linear range of 0.1–157.6 μM. This novel sensor system shows great potential application for GSH detection in blood serum sample and easyto-make analytical approaches in the future.

3.2 Bio-imaging

GQDs have a potential application in the field of bio-imaging because of their excellent fluorescence properties and the low cytotoxicity. GQDs were applied in cell imaging of human breast cancer cell line MCF-7 by Dong et al. [59]. The work shows that the cell membrane, cytoplasm, and nucleus can be marked with fluorescence by GQDs. It is the first time that the fluorescent carbon material has been used as fluorescent tags for a cell nucleus.

As we know, there had been no direct effective technology for imaging of stem cells for a long time, due to the particularity of the stem cells. It is significant that GQDs were used in imaging of stem cells by Zhang et al. [52] in order to solve this problem. Three different kinds of stem cells were cultivated with GQDs, and the results showed that GQDs can smoothly enter into the stem cells. It was found that GQDs were not observed in the nucleus, indicating that it will not cause genetic disruption of the stem cells. It showed that GQDs had relatively low cytotoxicity. In contrast, when stem cells were mixed with CdS quantum dots, it soon died, due to the toxicity of the heavy metals Cd²⁺. This approach demonstrates the distinctive advantages of GQDs for direct and efficient stem

cell labeling, opening up great opportunities for their biomedical applications.

Wang et al. [119] reported the first realization of the industrial-scale (20 l) production of high-quality fluorescent GQDs via a molecular fusion route from a low-cost, active derivative of pyrene. The as-prepared GQDs show superior optical properties including strong excitonic absorption bands extending to ~530 nm, bright PL at 510 nm with a quantum yield of up to 42%, and a wide PL spectrum. The GQDs are applied as biological fluorescent probes for visualizing and targeting the Golgi apparatus in HeLa and MCF7 live cells. The low-cost mass production, excellent biocompatibility, and superior optical properties make the GQDs an attractive alternative probe for efficient Golgi-targeted imaging in biomedical applications.

Ge et al. [120] presented a new photodynamic therapy (PDT) agent based on GQDs that can produce singlet oxygen (102) via a multistate sensitization process, resulting in a quantum yield of 1.3, the highest reported for PDT agents. The GQDs also exhibit a broad absorption band spanning the UV region and the entire visible region and a strong deep-red emission. Through *in vitro* and *in vivo* studies, they demonstrate that GQDs can be used as PDT agents, simultaneously allowing imaging and providing a highly efficient cancer therapy. The present work may lead to a new generation of carbon-based nanomaterial PDT agents with overall performance superior to conventional agents in terms of 102 quantum yield, water dispersibility, photo- and pH-stability, and biocompatibility.

In the work of Su et al. [121], the design of a peptide with trifunctional motifs is reported as the precursor building block for constructing a novel multifunctional protein nanofiber (PNF) and further conjugated with highly fluorescent GQDs by noncovalent interactions. The GQDs essentially maintain their favorable optical properties in the PNF-GQD nanohybrids. A good biocompatibility of the PNF-GQD nanohybrids is found with cell viability assays. With both a recognition moiety (RGD) and an imaging probe (GQD), these PNF-GQD nanohybrids possess the capability of targeting and imaging tumor cells simultaneously. This research demonstrates that GQD-decorated PNF nanohybrids have great potential as multifunctional platforms for biomedical applications, particularly, where the capability of sensitive tracking and efficient labeling is appreciated.

3.3 Drug delivery

There have been reports that graphene or graphene-based nanomaterials are utilized as carriers for delivery of drugs to improve the delivery efficiency or offer benefits in the therapeutic effect [122, 123]. Compared to graphene, GQDs have the better water solubility, lower cytotoxicity, and larger specific surface area, and also can combine with a variety of compounds through the intermolecular π - π interaction. Therefore, GQDs are the more effective carriers or loaders of drug molecules. For instance, a biocompatible and cell traceable drug delivery system based on GQD, for the targeted delivery of the DNA-intercalating drug doxorubicin (DOX) to cancer cells, was reported by Iannazzo et al. [124]. The GQDs were covalently linked to the tumor-targeting module biotin (vitamin K or vitamin B7), able to efficiently recognize biotin receptors overexpressed on cancer cells by means of a strategically designed cleavable linker, which can be specifically activated inside cells. The therapeutic agent used in this study, DOX, was loaded to the GQD surface, taking advantage of the excellent absorption properties of carbon nanomaterials, by π - π interaction. Moreover, the inherent fluorescence allowed the drug release to be tracked (Figure 19). This study has designed a new biocompatible and cell-traceable drug delivery system, able to release the therapeutic agent to cancer cells in a selective manner and minimize the anticancer drug systemic toxicity and undesirable side effects, typically associated with conventional chemotherapy.

In the study of Ghanbari et al. [125], blue fluorescent nitrogen-doped GQDs (N-GQDs) were synthesized by a

hydrothermal method via pyrolysis of citric acid as the carbon source and urea as the nitrogen source. For the first time, the N-GQDs have been loaded with the anticancer drug, methotrexate (MTX), to prepare the MTX-(N-GQDs) as an efficient drug delivery system. The *in vitro* cytotoxicity of the MTX-(N-GQDs) on human breast cancer cells investigated suggests that the drug-free N-GQDs nanocarriers are highly biocompatible, whereas the MTX-loaded ones are more cytotoxic than the free MTX. This research confirms the accomplishment of GQDs as nanocarriers to prolong the cytotoxic effects of its loaded drug for the better killing of cancer cells.

Significantly, a size-changeable GQD nanoaircraft (SCNA) that served as a hierarchical tumor-targeting agent with a high cargo payload was developed to penetrate and deliver an anticancer drug into deep tumors [126]. The nanoaircraft is composed of ultrasmall GQDs (less than 5 nm) functionalized with a pH-sensitive polymer that demonstrates an aggregation transition at a weak acidity of the tumor environment but is stable at physiological pH with stealth function. A size conversion of the SCNA at the tumor site is further actuated by near-infrared irradiation, which disassembles 150 nm of SCNA into 5 nm of DOX/GQD like a bomb-loaded jet, facilitating the penetration into the deep tumor tissue. At the tumor, the penetrated DOX/GQD can infect neighboring cancer cells for repeated cell killing. Such an SCNA integrated with combinational therapy successfully suppresses xenograft



Figure 19: GQD for tumor-targeted DOX delivery (reprinted/reproduced with the permission of Ref. [124], copyright 2017, Elsevier B.V.).

tumors in 18 days without distal harm. This work presents a sophisticated strategy, which displays the hierarchically targeted and penetrated delivery of drugs and energy to deep tumor and shows potential for use in other tumor therapies.

3.4 Solar cells

Solar cells are one of the hot research topics in the field of clean energy. The major factor for the use of GQDs in solar cells is the size-dependent bandgap tuning property. The GQDs have very attractive benefits for applications in solar cells compared with other materials such as silicon and perovskite, mainly because of better dispersion, the band gap which can be regulated, high chemical stability, and low toxicity. Additionally, GQDs have the quantum confinement effect and edge effect, well suited to solar cells. To date, many kinds of GQD-based solar cells have been reported, such as the use of hole transport layer (HTL) material [127], silicon/GQD heterojunction solar cell [128], semiconductor/GQD solar cell [129], and conductive polymer-doped GQD solar cell [130]. Most researches have focused on the use of GQDs as an electron-hole transfer material and as a tuner of the band gap.

In the work of Li et al. [131] derived from doublewalled CNTs, GQDs with a uniform size distribution were prepared through solution chemistry. The GQDs in chlorobenzene exhibit bright blue emission upon UV excitation. The introduction of the GQDs into a bulk heterojunction polymer solar cell (PSC) based on poly(3hexylthiophene):(6,6)-phenyl-C61 butyric acid methyl ester (P3HT:PCBM) results in a significant enhancement of the power conversion efficiency (PCE). The efficiency can be further improved by adjusting the PCBM content in the active layer, reaching a maximum PCE of 5.24%. This ternary system based on blended P3HT:PCBM:GQDs represents a new method to enhance the efficiency of PSC. This work expands the application of GQDs to PSC devices.

Kundu et al. [132] reported an enhanced PCE of $11.7\% \pm 0.2$ and a fill factor (FF) of 71% for dye-sensitized solar cells (DSSC) with an active area of 0.16 cm^2 after modifying the TiO₂ photoanode with size-selective (ca. 2 nm) N,F,S-codoped GQDs (NFS-GQDs), which exhibit a PL quantum yield of 70%. An upward shift in the Fermi level has been observed, perhaps responsible for the improved performance along with the possibility of preventing the back electron transfer from TiO₂. This work indicates that the incorporation of size controlled, hetero atom-doped GQDs can enhance the efficiency of DSSCs, enabling more opto-electronic applications.

Besides the above applications, research has progressed step by step until now, and the GQDs are applied in materials or various complex devices, such as catalysts [133, 134], photovoltaic devices [135, 136], LEDs [137], lithium ion batteries [138], supercapacitors [139, 140], photodetectors [141, 142], tissue-engineering materials [143], etc.

4 Conclusions and outlook

As discussed in this article, many kinds of preparation methods of GQDs are developed. The basic concept and classical method for making GQDs is cleavage of carbonaceous materials by repeated oxidation and reduction. Besides, there are other ways including controllable synthesis and carbonization. At present, the hydrothermal process using GO as a starting material to obtain GQDs is the environmentally friendly approach, and strong-acidic treatment of graphite is the method which can achieve mass production. For further development of the GQDs, we need to find the commercially available and effective methods to fabricate various GQDs. Devices and applications can benefit from the GQDs because of their special optical and electrical properties. Promising strategies have been provided by elaborate designs of micro-structures and device structures for practical applications and future researches. However, the research on the GQDs is still in its early stage compared to graphene. There is still a long way to go for extensive practical applications, and there is also a wide space of exploration for researchers.

First, there are still many issues waiting to be settled for further development. For instance, it is still a challenge to find scaled but facile synthetic methods for the production of GQDs with high quality, though much research on the fabrication methods has been published. Furthermore, conclusive evidence and convincing explanation for the PL mechanism of GQDs are still absent. In addition, it is still unclear how the factors, such as size, doping, crystallinity, and surface functionalization, have influence on the optical properties. Moreover, both indepth experimental verification and theoretical calculations are much desired. For example, a catalytic model should provide a conceptual framework to help understand how GQDs and active components interact. It is also important to determine the types of defects or sites that are most appropriate for tuning the interactions and how this can affect the reaction mechanism. All of the issues inhibit the development of GQDs.

Additionally, further researches for potential applications are also important and must be paid more attention, besides the fundamental studies. For application in bio-imaging in vivo and in vitro, long-wavelength emission or up-conversion luminescence is more appropriate for the biological window. However, quantum yield of GQDs is often low when excited with long wavelength light. Furthermore, most of the GQDs exhibit bright blue to green luminescene, but high efficient long-wavelength emission is still absent to obtain WLEDs with high color rendering index (CRI), as well as warm white light. It is suggested that large sp² domain is favorable for yellow and red emission, but the method is of low efficiency [144]. Therefore, new methods for large-scale production of GQDs with long emission wavelengths are expected. Additionally, though GQDs are expected to play an important role in novel devices, such as photovoltaic devices, the synthetic variability hinders reproducibility and affects the efficiency. The size and surface molecules need to be fine tuned if efficient devices are to be prepared. All of these issues are waiting to be settled for further development. We hope further researches can successfully solve the problems in the near future. Under the joint efforts of researchers, we believe that not only novel preparation methods and properties of GQDs will be found, but also new devices and applications will be invented.

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