Graphene Quantum Dots (GQDs) and their Synthesis: A Critical Review

Dr. (Smt.) Rashmi Jindal
Assistant Professor, Chemistry Department, C. L. Jain Degree College, Firozabad, UP, India

Being a fluorescent carbon material, graphene quantum dots (GQDs) have seeked attention due to their properties and potential applications in biological, optoelectronic, and energy-related fields. Furthermore, GQDs are nontoxic and possess biologically inert properties. Due to these characteristics, they are apt for various commercial and domestic applications, which include catalysis, imaging, medical applications, energy-based research, and environmental applications.

However, their high cost and low yield remain open challenges for practical applications. Many carbon-based resources has been used to synthesise GQDs, such as graphite flakes, carbon nanotubes, graphene, carbon fibrecoal and others. The main focus of this review is on the methods of synthesis of GQDs. The synthesis strategies of GQDs, including top–down and bottom–up strategies mainly containing, the hydrothermal or solvothermal method, the ultrasonic-assisted or microwave assisted process and electrochemical oxidation from small molecules or polymers, are discussed.

Keywords: Graphene Quantum Dots, Bottom-up method, Top-down method.

1. INTRODUCTION

Over the past two decades, nanostructured semiconductors, or quantum dots (QDs), have garnered significant attention due to their size-dependent optoelectronic properties. Since graphene's discovery in 2004, metal-free carbon-based QDs, such as carbon QDs (CQDs), graphene quantum dots (GQDs), and graphitic-carbon nitride QDs (g-CNQDs), have emerged as promising alternatives to traditional metallic QDs. These carbon-based QDs not only retain the excellent stability and tunable fluorescence of metallic QDs but also offer additional benefits such as easy synthesis, superior biocompatibility, and low toxicity.

GQDs, a recently discovered type of carbon-based nanomaterial, are derived from two-dimensional graphene, which restricts electronic transport in all three spatial dimensions. With diameters of less than 20 nanometers, GQDs are small enough to confine excitons, exhibiting a non-zero band gap that becomes luminescent when stimulated. Compared to carbon nanodots, GQDs have superior chemical and physical properties, including a higher length-to-diameter ratio, larger surface area, and stronger surface bonding due to their graphene layer structure. Additionally, GQDs possess the attractive property of photoluminescence (PL), attributed to quantum confinement.

When ideal graphene is transformed into GQDs, the band gap becomes adjustable. The structure of GQDs depends on the synthesis and doping methods used to modify the band gap. It was studied that theoretical analysis on the impact of zigzag edges on the PL properties of GQDs of different sizes, ranging from approximately 0.46 to 2.31 nm, covering wavelengths from ultraviolet (UV) to infrared. They found that the band gap distance is inversely proportional to the size of the GQD, meaning smaller GQDs have larger band gaps. By manipulating the size and surface chemical groups of GQDs, it is possible to regulate their band gap energy within a range of 0 to 6 electron volts.

GQDs exhibit two key characteristics: edge effects and quantum confinement. These mechanisms enable GQDs to possess unique electrical, optical, and structural properties not found in other nanomaterials. GQDs with functionalized edges containing groups like epoxy, carboxyl, hydroxyl, and carbonyl can interact with biological molecules such as enzymes, proteins, or antibodies. They have been successfully conjugated with antibodies and DNA molecules through amide coupling, making them valuable for creating high-sensitivity nanomaterials and diagnostic tools. The crystal lattice structure of GQDs, resembling a honeycomb with sp2-hybridized carbon atoms, allows for electron delocalization in the π-orbitals, influencing their PL behavior and edge shapes (zigzag or armchair).

Furthermore, GQDs are known for their low toxicity, good solubility, stable fluorescence, chemical inertness, and surface grafting capabilities. These quantum properties make GQDs suitable for various applications, including biological imaging, light-emitting diodes, photoelectrocatalysis, drug carrier sensors, and pollutant absorption. One of the most appealing aspects of GQDs is their abundance as carbon materials, which can be functionalized at their edges, making them more advantageous than mineral QDs. GQDs have also demonstrated antimicrobial properties, with the first modification of GQD properties through nitrogen doping studied by previous researchers.

Graphene, discovered by Novoselov et al. in 2004 [1], is a new type of nanomaterial with good mechanical, electrical, thermal and optical properties [2-5], with zero-dimensional fullerenes [6] and the one-dimensional carbon nanotubes [7]. With time, QDs obtained from different materials have increased focus in many research fields, such as solar cells, optoelectronic transistor components, and fluorescent biological labels because of their unique size-tunable optical and electronic properties [8]

Graphene quantum dots (GQDs), a latest zero-dimensional (0D) member of the carbon family, consist of single to few layers of graphene sheets with lateral dimensions of <10nm [9] and excellent chemical [10], physical [11],and biological properties [12,13]. Generally, GQDs have the interesting properties derived from two-dimensional (2D) graphene and also show remarkable physicochemical properties of the QDs, including edge effects, non-zero band gap, and quantum confinement effects, by which they have great potential in energy, electronic, and optical industry[14]. Studies prove that GQDs have good biocompatibility [15] and low biotoxicity [16].

Strictly, GQDs have a single atomic layer and only contain carbon. The GQDs prepared contain oxygen and hydrogen, and generally have multiple atomic layers, with sizes being less than 10 nm [17]. The functionalized GQDs have been used as a reagent and an effective acidic nano-catalyst for obtaining the xanthene derivatives [18]. Currently, a lot of research is done on the surface chemical modification of the GQDs to regulate the properties for the applications [19] and shown a significant impact of GQDs in medicine. The studies have shown synthesis of novel GQDs methods from simple “one-pot” solutions and the utilization of more molecules such as glucose and citric acid, as opposed to graphene and graphite [20]. Thus, GQDs/GOQDs have a great use in optical and electrochemical sensing [21], photovoltaics, photocatalysis, bioimaging [22], biosensing [23] light-emitting diodes, and so on.

2. SYNTHESIS OF GRAPHEENE QUANTUM DOTS

The methods for GQDs synthesis can be divided into top-down and bottom-up processes as shown in Figure 1 [24].

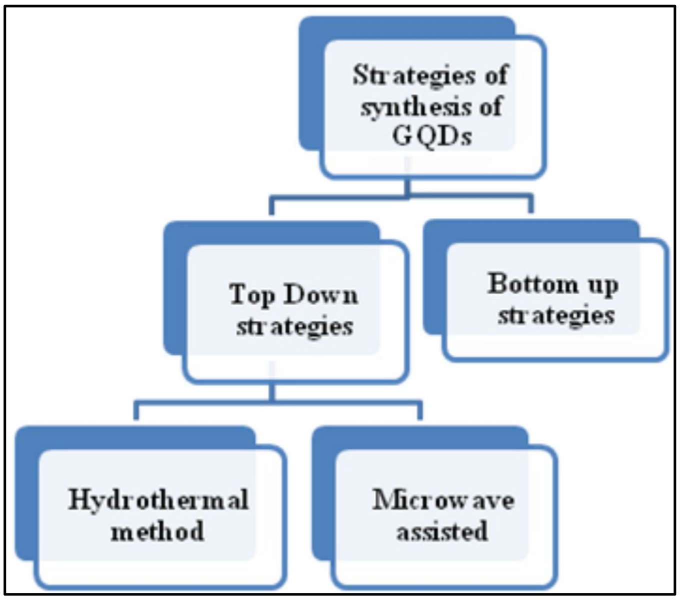

Fig.1: Two main approaches were adopted to prepare GQDs: the top-down and bottom-up method.

2.1. Top Down Synthesis

In this method, destructive approach is employed. The larger molecules broken down, into smaller units and these molecules are converted into suitable NPs. Examples of this method are grinding/milling, CVD, physical vapor deposition (PVD) and other decomposition techniques [25]. There are many methods for GQDs synthesis based on top-down processes, including chemical oxidation method [26], hydrothermal method [27], ultrasonic assisted method [28] electrochemical oxidation method [29] chemical vapor deposition (CVD) method [30] pulsed laser ablation (PLA) technique [31], or a combination of the above processes [32].

2.2. Bottom Up Synthesis

The bottom-up approach involves the synthesis of the GQDs from small molecular precursors, and benzene derivatives are condensed to form bigger molecules, having well-defined size, shape, and desirable properties [33] In the bottom-up methods, solution-based chemical methods allow the synthesis of GQDs starting from several types of organic precursors; such as malic acid, urea and other organic precursors [34]. A number of precursors, including organic salts, ethanolamine, acetylacetone, amino acids, co-factors (ascorbic acid), humic acid, coffee grounds, carbohydrates (sucrose or glucose), citric acid, etc., have been used for the bottom–up preparation of GQDs [35].

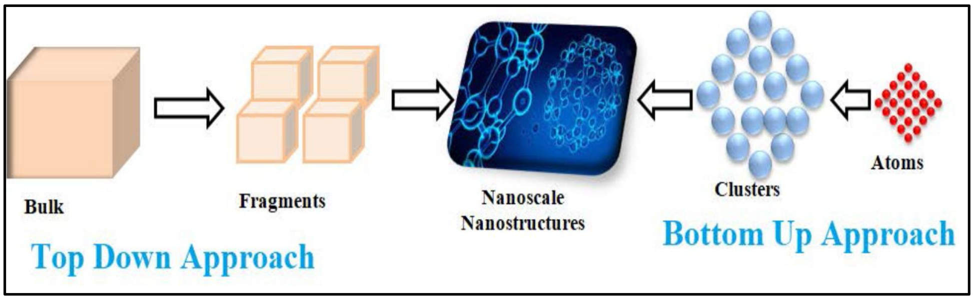

Fig. 2: The schematic representation of the top-down and bottom-up approaches for the fabrication of metal oxide nanostructures.

2.3. Microwave Assisted Method

Microwave (MW)-assisted synthesis is easy and quick technique as an alternative energy input source and has been widely used because of its control for internal and volumetric heating of materials [36]. The, graphene were oxidized in absorption of MW irradiation by one component of the reaction has enclosed this method of synthesis within the concept of green chemistry; added advantages are the synergy with green solvents and solvent-free conditions [37].

2.4. Hydrothermal Synthesis

The hydrothermal or solvo-thermal method is a simple and quick method for the preparation of GQDs. It cut carbon materials into GQDs under the conditions of high temperature and high pressure in the process. Before the reactions the carbon materials need to be treated through strong oxidation [38]. The principle is to break the bonds between carbon materials to form GQDs with high temperature under high pressure [39]. The, large graphene sheets were oxidized concentrated H_2SO_4 and HNO_3 to form GODs, introducing oxygen-containing functional groups in the edge and basal plane of the graphene sheets. The defect-rich GO was then dispersed in an aqueous NaOH solution and treated in an autoclave reactor at 200 °C. The solution was dialyzed through a 0.22 μm membrane to separate the GQDs from the remaining bulk graphene precursor, and the resulting GQDs had a 9.6 nm average diameter and displayed strong blue fluorescence [40]. Recently, Wang et al. prepared sulfurdoped GQDs (S-GQDs) by one pot hydrothermal exfoliation reaction in contrast to the GQDs [41].

2.5. Ultrasonic Assisted Method

Ultrasonic techniques for the synthesis of GQDs involve the use of intense ultrasound under drastically high temperature and pressure conditions in order to avoid a long reaction time for designing nanocarbon particles [42]. Gao et.al prepared three kinds of GQDs of pristine graphene quantum dots (PGQDs), expanded graphene quantum dots (EGQDs) and graphene oxide quantum dots (GOQDs) using natural graphite, expanded graphite, and oxide graphite as the raw materials in a supercritical CO_2/H_2O system assisted by ultrasound [43].

2.6. Electrochemical Oxidation Method

In electrochemical exfoliation, layered bulk materials, such as graphite rods, are treated with the aid of an applied electric field. In the electrochemical oxidation method process, carbon–carbon bonds of graphite, graphene, or carbon nanotubes are oxidized and decomposed into GQDs at a high redox voltage (+1.5 to +3 V) [44].

3. CONCLUSION

In this paper, an overview about the synthesis of GQDs is presented. For further development of the GQDs, we need to find the commercially available and effective methods to create various GQDs. The recent progress in fabrication strategies including top–down and bottom–up has been critically reviewed. Devices and applications can benefit from the synthesis of GQDs because of their special optical and electrical properties. Many synthesis methods have been provided elaborately which help in designing 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 synthesis, and there is also a wide space of exploration for researchers.

REFERENCES

[1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jhang, Y. Jhang, S.V. Dubonos, I.V. Grigorieva and A.A. Firsov; “Electric field effect in atomically thin carbon films”, Science, Vol. 306(5696), pp. 666–669, 2004.

[2] A.K. Geim; “Graphene: status and prospects”, Science, Vol. 324(5394), pp. 1530–1534, 2009.

[3] K.I. Bolotin, K.J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim and H.L. Stormer; “Ultrahigh electron mobility in suspended graphene”, Solid State Commun., Vol. 146(9-10), pp. 351–355, 2008.

[4] L. Jiao, X. Wang, G. Diankov, H. Wang and H. Dai; “Facile synthesis of high-quality graphene nanoribbons”, Nat. Nanotechol., Vol. 5, pp. 321-325, 2010.

[5] X.Z. Xu, J. Zhou, J. Jestin, V. Colombo and G. Lubineau; “Preparation of water-soluble graphene nanoplatelets and highly conductive films”, Carbon, Vol. 124, pp. 133–141 2017.

[6] L. Du, X. Luo, F. Zhao, W. Lv, J. Zhang, Y. Peng, Y. Tang and Y.Wang; “Toward facile broadband high photoresponse of fullerene based phototransistor from the ultraviolet to the near-infrared region”, Carbon, Vol. 96, pp. 685–694, 2016.

[7] C. Qiu, Z. Zhang, M. Xiao, Y. Yang, D. Zhong and L.M. Peng; “Scaling carbon nanotube complementary transistors to 5-nm gate lengths”, Science, Vol. 355(6322), pp. 271–276, 2017.

[8] R. Das, R. Bandyopadhyay and P. Pramanik; “Carbon quantum dots from natural resource: A review”, Mater. Today Chem., Vol. 8, pp. 96-109, 2018.

[9] S. Benítez-Martínez and M. Valcárcel; “Graphene quantum dots in analytical science”, TrAC Tr. Anal. Chem., Vol. 72, pp. 93–113, 2015.

[10] L. Jiao, L. Zhang, X. Wang, G. Diankov and H. Dai; “Narrow graphene nanoribbons from carbon nanotubes”, Nature, Vol. 458, pp. 877–880, 2009.

[11] D.V. Kosynkin, A.L. Higginbotham, A. Sinitskii, J.R. Lomeda, A. Dimiev, B.K. Price and J.M. Tour; “Longitudinal unzipping of carbon nanotubes to form graphene nanoribbons”, Nature, Vol. 458, pp. 872–876, 2009.

[12] S. Bak, D. Kim and H. Lee; “Graphene quantum dots and their possible energy applications: A review”, Curr Appl Phys., Vol. 16(9), pp. 1192–1201, 2016.

[13] P.Zheng and N. Wu; “Fluorescence and sensing applications of graphene oxide and graphene quantum dots: a review”, Chem An Asian J., Vol. 12(18), pp. 2343–2353, 2017.

[14] X. Zhao, W. Gao, H. Zhang, X. Qiu, Y. Luo; “20-Graphene quantumdots in biomedical applications: recent advances and future challenges”, Handbook Nano. Anal. Chem., ISBN 9780128166994, 2020.

[15] H. Singh, S. Sreedharan, K. Tiwari, N.H. Green, C. Smythe, S.K. Pramanik, J.A. Thomas and A. Das; “Two photon excitable graphene quantum dots for structured illumination microscopy and imaging applications: lysosome specifcity and tissue-dependent imaging”, Chem Commun., Vol. 55, pp. 521–524, 2019.

[16] F. Nasrollahi, Y.R. Koh, P. Chen, J. Varshosaz, A.A. Khodadadi and S. Lim; “Targeting graphene quantum dots to epidermal growth factor receptor for delivery of cisplatin and cellular imaging”, Mater Sci Eng C, Vol. 94, pp. 247–257, 2019.

[17] R. Liu, D. Wu, X. Feng and K Mullen; “Bottom-up fabrication of photoluminescent graphene quantum dots with uniform morphology”, J. Am. Chem. Soc, Vol. 133(39), pp. 15221–15223, 2011.

[18] A. Shomali, H. Valizadeh, A. Banan and R. Mohammad-Rezaei; “Efficient synthesis of xanthene derivatives using carboxyl functionalized graphene quantum dots as an acidic nanocatalyst under microwave irradiation”, RSC Advances, Vol. 5(107), pp. 88202-88208, 2015.

[19] D. Yu, X. Zhang, Y. Qi, S. Ding, S. Cao, A. Zhu and G. Shi; “Pb2+-modified graphene quantum dots as a fluorescent probe for biological aminothiols mediated by an inner filter effect”, Sens. Actuators B: Chem., Vol. 235, pp. 394–400, 2016.

[20] S. Liu, J. Cui, J. Huang, B. Tian, F. Jia and Z. Wang; “Facile one-pot synthesis of highly fluorescent nitrogen-doped carbon dots by mild hydrothermal method and their applications in detection of Cr (VI) ions", Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Vol. 206, pp. 65-71, 2019.

[21] L. Li, G. Wu, G. Yang, J. Peng, J. Zhao and J.J. Zhu; “Focusing on luminescent graphene quantum dots: current status and future perspectives”, Nanoscale, Vol. 5(10), pp. 4015−4039, 2013.

[22] M. Bacon, S.J. Bradley and T. Nann; “Graphene quantum dots”, Part. Syst. Charact., Vol. 31(4), pp. 415−428, 2014.

[23] J. Wen, Y. Xu, H. Li, A. Lu, and S. Sun; “Recent applications of carbon nanomaterials in fluorescence biosensing and bioimaging”, Chem. Commun., Vol. 51(57), pp. 11346−11358, 2015.

[24] M.J. Sweetman, S.M. Hickey, D.A. Brooks, J.D. Hayball and S.E. Plush; “A practical guide to prepare and synthetically modify graphene quantum dots”, Adv Func Mater., Vol. 29(14), 2019, 1808740.

[25] S. Iravani; “Green synthesis of metal nanoparticles using plants”, Green Chem., Vol. 13(10), pp. 2638-2650, 2011.

[26] S. Wang, K. Zhang, Q. Wang, Y. Fan, J. Shen, L. Li, L. Yang and W. Zhang; “Graphene quantum dot-assisted preparation of water-borne reduced graphene oxide/polyaniline: from composite powder to layer-by-layer self-assembly flm and performance enhancement”, Electrochim Acta., Vol. 295, pp. 29–38, 2019.

[27] P. Luo, X. Guan, Y. Yu, X. Li and F. Yan; “Hydrothermal synthesis of graphene quantum dots supported on three-dimensional graphene for supercapacitors”, Nanomaterials, Vol. 9(2), pp. 201, 2019.

[28] A. Shukla, P. Dhanasekaran, N. Nagaraju, S.D. Bhat and V.K. Pillai; “A facile synthesis of graphene nanoribbon-quantum dot hybrids and their application for composite electrolyte membrane in direct methanol fuel cells”, Electrochim Acta., Vol. 297, pp. 267–280, 2019.

[29] Y. Li, S. Li, Y. Wang, J. Wang, H. Liu, X. Liu, L. Wang, X. Liu, W. Xue and N. Ma; "Electrochemical synthesis of phosphorus-doped graphene quantum dots for free radical scavenging", Phys Chem Chem Phys., Vol. 19(18), pp. 11631–11638, 2017.

[30] M.J. Deka and D. Chowdhury; "CVD assisted hydrophobic graphene quantum dots fuorescence sensor for aromatic amino acids", Chemistry Select, Vol. 2(5), pp. 1999–2005, 2017.

[31] R.L. Calabro, D.S. Yang and D.Y. Kim; "Liquid-phase laser ablation synthesis of graphene quantum dots from carbon nano-onions: Comparison with chemical oxidation", J Colloid Interface Sci., Vol. 527, pp. 132–140, 2018.

[32] S. Zhuo, M. Shao and S.T. Lee; "Upconversion and downconversion fuorescent graphene quantum dots: ultrasonic preparation and photocatalysis", ACS Nano., Vol. 6(2), pp. 1059–1064, 2012.

[33] J. Wu, W. Pisula and K. Mullen; "Graphenes as potential material for electronics", Chemical Reviews, Vol. 107(3), pp. 718–747, 2007.

[34] M. Jorns and D. Pappas; "A review of fluorescent carbon dots, their synthesis, physical and chemical characteristics, and applications", Nanomaterials, Vol. 11(6), pp. 1448, 2021.

[35] S. Zhou, H. Xu, W. Gan and Q. Yuan; "Graphene quantum dots: recent progress in preparation and fluorescence sensing applications", RSC Adv., Vol. 6(112), pp. 110775–110788, 2016.

[36] P.B. Agranovich, G. Ishai, D. Katz, D. Bezman and Y. Feldman; "Microwave dielectric spectroscopy study of water dynamics in normal and contaminated raw bovine milk", Colloids Surfaces B: Biointerfaces, Vol. 154, pp.391-396, 2017.

[37] P. Piyasena, C. Dussault, T. Koutchma, H.S. Ramaswamy and G.B. Awuah; "Radio Frequency Heating of Foods: Principles, Applications and Related Properties-A Review", Crit. Rev. Food Sci. Nutr., Vol. 43(6), pp. 587–606, 2003.

[38] H. Tetsuka, R. Asahi, A. Nagoya, K. Okamoto, I. Tajima, R. Ohta and A. Okamoto; "Optically tunable amino-functionalized graphene quantum dots", Advanced Materials (Deerfield Beach, Fla.), Vol. 24(39), pp. 5333–5338, 2012.

[39] L. Wang, B. Wu, W. Li, S. Wang, Z. Li, M. Li, D. Pan and M. Wu; "Amphiphilic graphene quantum dots as self-targeted fuorescence probes for cell nucleus imaging", Adv Biosyst., Vol. 2(8), pp. 1700191, 2018.

[40] D. Pan, J. Zhang, Z. Li, and M. Wu; "Hydrothermal route for cutting graphene sheets into blue-luminescent graphene quantum dots", Adv. Mater., Vol. 22(6), pp. 734-738, 2010.

[41] G. Wang, Q. Guo, D. Chen, Z. Liu, X. Zheng, A. Xu, S. Yang and G. Ding; “Facile and highly effective synthesis of controllable lattice sulfur-doped grapheme quantum dots via hydrothermal treatment of durian”, ACS Appl. Mater. Interf., Vol. 10(6), pp. 5750–5759, 2018.

[42] V.B. Kumar, J. Tang, K.J. Lee, V.G. Pol and A. Gedanken; “In Situ Sonochemical Synthesis of Luminescent Sn@C-Dots and a Hybrid Sn@C-Dots@Sn Anode for Lithium-Ion Batteries”, RSC Adv., Vol. 6(70), pp. 66256–66265, 2016.

[43] H. Gao, C. Xue, G. Hu and K. Zhu; “Production of graphene quantum dots by ultrasoundassisted exfoliation in supercritical CO2/H2O medium”, Ultrason Sonochem., Vol. 37, pp. 120–127, 2017.

[44] Y. Li, S. Li, Y. Wang, J. Wang, H. Liu, X. Liu, L. Wang, X. Liu, W. Xue and N. Ma; “Electrochemical synthesis of phosphorus-doped graphene quantum dots for free radical scavenging”, Phys. Chem. Chem. Phys., Vol. 19(18), pp. 11631–8, 2017.