UNIVERSITI MALAYSIA PERLIS
International Journal of Nanoelectronics and Materials
IJNeaM
ISSN 1985-5761 | E-ISSN 2232-1535

Synthesis of graphene quantum dots via one step hydrothermal cutting: The synergistic effect of graphene oxide and sodium hydroxide

Aida Zulia Zulhanip[a], Nor Shahanim Mohamad Hadis[a]*, Afaf Rozan Mohd Radzol[a], Zurita Zulkifli[b], Anis Diyana Rosli[a]

[a]*Electrical Engineering Studies, Universiti Teknologi MARA, Cawangan Pulau Pinang, Permatang Pauh Campus, 13500 Permatang Pauh, Pulau Pinang, Malaysia*
[b]*Faculty of Electrical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor Darul Ehsan, Malaysia*
**Corresponding author. E-mail: norsh713@uitm.edu.my*

Received 16 January 2025, Revised 2 May 2025, Accepted 2 July 2025

ABSTRACT

This study reports a one-step hydrothermal cutting method of synthesizing graphene quantum dots (GQDs) using commercially available, 4–10% edge oxidized precursor graphene oxide (GO). The controlled properties of synthesized GQDs formation on the treatment solely with alkali additives, sodium hydroxide (NaOH), act as alkaline-induced fragmentation and surface modifier to perform a surface functionalization. No additional hazardous chemicals were used during the synthesis process, contributing to the cost-effectiveness and simplicity of the GQDs formation and eco-friendly nature processes. Additionally, non-doped GQDs were synthesized at quantitative parameters: NaOH concentration (0.1 M), temperature (200 °C), and reaction time (24 h), that can achieve effective performance characteristics for sensing platforms. The synergistic mechanism between GO and NaOH in synthesizing GQDs involves three key processes: i) pre-treatment with NaOH, ii) hydrothermal cutting, and iii) reduction by NaOH. The GQDs were through the characterization process to trace the transformation using different analytical techniques such as ultra-high resolution scanning electron microscope (UHR-SEM), energy-dispersive x-ray spectroscopy (EDX), transmission electron microscope (TEM), photoluminescence spectroscopy (PL), x-ray diffraction (XRD), ultraviolet-visible spectroscopy (UV-Vis), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), and zeta potential to confirm their structural, optical, and surface characteristics. The finding demonstrated that NaOH-mediated hydrothermal cleavage without hazardous reagents, offering an eco-friendly approach, and successfully synthesized non-doped GQDs at average size of ~1.3 nm which led to an impressive enhancement in optical performance. The high oxygen content and surface functionality in synthesized GQDs were believed to provide active sites for molecule binding potentially used in sensing applications particularly in heavy metal ion detection, as evidenced by comprehensive analytical characterization.

Keywords: *Graphene quantum dots (GQDs), Graphene Oxide (GO), Hydrothermal cutting, Sodium hydroxide (NaOH), Analytical characterization.*

1. INTRODUCTION

Graphene Quantum Dots (GQDs) have emerged as a new class of zero-dimensional (0D) nanomaterials with graphitic structures. The GQDs is a type of nanomaterial obtained from the fragmentation of graphene or carbon-based materials that exhibits fascinating optical, electrical, and chemical properties distinct from bulk graphene [1]. The GQDs merge the unique properties of graphene and quantum dots with a size dimension lower than 10 nm [2], making them significantly smaller than graphene sheets. The smaller size of GQDs leads to the quantum confinement effect and thus contributes to the discrete energy level.

The GQDs have gained attention as highly promising nanomaterials with cutting-edge applications. They generally fascinated researchers worldwide and have been recognized for their unique properties, such as determined photoluminescence, tuneable bandgap, non-toxicity and biocompatibility, high surface area, and adequate chemical stability [3]. Due to the distinctive characteristics of GQDs, it opens the door for diverse applications and potential fields such as biomedical imaging, energy storage, environmental monitoring and recovery, and catalysis.
The promising potential and versatility for sustainable applications, realizing a wide range of uses for GQDs highlight the importance of developing simple and scalable techniques to fully achieve their benefits. The easily scalable for mass production serves to minimize environmental impact and ensures reproducibility, consistency, and quality control.

The top-down and bottom-up approaches are initiated to investigate the strategies for synthesizing GQDs. The top-down process is considered a breaking down or cutting process of bulk materials into nanoscale fragments such as graphite, carbon sources, and graphene oxide. It leads to prominent chemical synthesis techniques, i.e., chemical oxidation and exfoliation and solution-based synthesis of hydrothermal, solvothermal, and liquid phase exfoliation.

The bottom-up process involves the construction of complex structures that begins with single atoms or small precursor molecules such as amino acids or small sugar molecules, citric acid, tannic acid [4], and hexa-perihexabenzocoronene [5] as a raw material, which are controlled by chemical reactions and carbonization.

Hydrothermal synthesis provides eco-friendliness, simplicity, and scalability in production compared to other conventional chemical synthesis methods. The hydrothermal method, performed in a closed system using water as a solvent, can provide an environmentally friendly setup by minimizing the use of toxic reagents. Besides, the key factors in the morphology control, such as high temperature and pressure, enhance the reaction kinetics, thus enabling tailored nanostructures [6].

1.1. Properties of Graphene Oxide

Graphene is a carbon allotrope that exists in a two-dimensional form. It possesses remarkable characteristics such as excellent conductivity, mechanical strength, and flexibility. Graphene offers a stable feature that makes it very suitable for a wide range of applications. Graphene Oxide (GO) is often associated with graphene and is usually portrayed as a fragile, flat, single layer of carbon atoms arrangement [7]. The GO can be obtained through the chemical process that indirectly introduces an oxygen-containing functional group to the graphene sheet.

The formation structure of GO is quite intricate, owing to the existence of specific functional groups and defects within the graphene lattice. The GO has a hexagonal lattice arrangement, with carbon atoms and oxygen functional groups forming a structure. The presence of an oxygen functional group modifies the properties of the material. GO is also known for its hydrophilic properties, which allow it to disperse naturally in water and other polar solvents [8]. A work by Mouhat F. et al. (2020) investigates the GO structure and behavior using first-principles molecular simulations. The distribution of oxygen-functional groups resembling hydroxyl and epoxide appears on the GO surface. The simulation reveals that the oxygen groups cluster together on the GO surface instead of dispersing uniformly, resulting in a water-attracting region for the GO. [9].

GO is widely used as a precursor for synthesizing graphene quantum dots (GQDs) due to its readily available availability, ease of functionalization, low toxicity, control size properties, and hydrophilic nature characteristics. The hydrophilic nature of GQDs is essential for specific implementations, especially involving interaction with water, such as medical, biological, and sensing applications. Several studies utilize GO as a precursor for the synthesized GQDs due to the yield of providing active sites for chemical reactions. GO is commonly handled by strong oxidizing or/and reducing agents to produce GQDs with oxygen groups [10].

Facure M.H.M. et al. (2022) produced luminescence GQDs by hydrothermal synthesis using GOs precursors by investigating the concentration, temperature, and pH of the GO solution [11]. After optimizing the synthesis condition (2 mg/mL, 175 °C, and pH 8), a relatively high quantum yield (QY) of 8.9% was achieved. This finding reveals that the amount of specific oxygen functionalities can be manipulated by controlling the synthesis parameters.

Mukherjee D. et al. (2022) highlight the different temperatures, i.e., 30, 50, and 110 °C of the synthesized GO, which possess different structural and functional properties [12]. GO's various temperatures were used as a source for GQDs. The GQDs exhibit a lessened particle size of 3.6 nm and QY of 64.8% of the synthesized GO-50. Such research studies were intensified by Pan et al. (2010), who developed a cutting mechanism for the GO sheets using hydrothermal to synthesize ultrafine GQDs with strong blue emission [13]. The structure of GQDs in alkali and acidic agents has been confirmed through the breakup of mixed epoxy (epoxy and carbonyl groups). Even though these graphene-based materials are promising for future nanodevices, their two-dimensional nature presents limitations due to poor control over the functionalization process, random surface functional group distribution [14], and synthesis complexity [15] for their implementation into advanced technological applications.

1.2. Graphene Oxide as a foundational substance

Graphene oxide (GO) is exceptional graphene-related nanomaterials. The synthesis of graphene quantum dots (GQDs) mainly begins with synthesizing GO. The attractive prospective precursor of GO can be used as the primary carbon resource in the synthesis process due to having many oxygen-containing functional groups (OH, COOH, and C-OH) on their basal planes and edges [16]. The presence of abundant oxygen-functional groups causes strong surface reactions. Recognizing that the presence of the functional groups is necessary for generating bright and tuneable fluorescent imaging [17]. A recent study involved GO as a versatile material in applications such as transition metal complexes, conducting polymer composites, catalysis, energy storage, optoelectronics, drug delivery, and bioimaging.

The hydrothermal method breaking the GO in a strong alkaline environment modifies the edge of the cutting part. Modifying GO can manipulate and improve the optical properties of GQDs through control conditions such as temperature and time reaction, precursor, surfactant, and reaction method. Being environmentally friendly is one of the advantages of using GO to synthesize GQDs, particularly as the use of highly toxic substances is avoidable.

1.3. Hydrothermal cutting process

The synthesis of GQDs via the hydrothermal cutting process using GO as the precursor materials offers a beneficial approach for the scalable production of high-quality GQDs with controllable optical and electrical properties. Compared to the other strategies, the hydrothermal method is undoubtedly simple, quick, and environmentally friendly compared to the other strategies [18]. The synthesis method assists the reduction and fragmentation process of GO through controlled parameters.

The advantage of this synthesis process is the production of high-yield GQDs, ensuring optimal utilization of the starting material. In addition, the GQDs display uniform size distribution, which is beneficial for a wide range of applications that demand precise size control. Furthermore, the reaction parameters, such as temperature, pressure, and the presence of additive solutions (chemicals, polymers, nanoparticles, and others), can be directly tailored to manipulate the physical properties of the synthesized GQDs.

1.4. Scope of Work

There is a need for scalable, eco-friendly and effective methods to synthesize GQDs as the demand for sensing application has grown. Despite the numerous existing synthesis strategies, multi-step processes and toxic chemicals requirements provide poor control over the size and surface functionality. This study focuses on a non-toxic method of synthesizing GQDs that adopts a one-step hydrothermal cutting for its simplicity, environmentally friendly manner, and high efficiency in producing functionalized GQDs using commercial GO and sodium hydroxide (NaOH) in a single step process.

NaOH has alkaline properties, selected due to its strong basicity and affordability as a sole additive cutting agent, effectively enabling the fragmentation of carbon networks and facilitating both the cutting and reduction of GO. This safer alternative to an eco-friendly synthesis avoids other alkaline solutions such as potassium hydroxide, KOH, or ammonium hydroxide, NH_4OH, ensuring the formation of quantum dots without introducing toxic residues. The safety of this approach is the main advantage compared to other methods involving toxic substances. Although NaOH is widely utilized in synthesis-based graphene material, the complex interaction mechanism between NaOH and GO during the cutting process remains insufficiently clarified. The existing studies include other dopants or reducing agents, which makes it hard to isolate the role of NaOH as surface-modifying separately.

Here, the synergistic interaction between GO and NaOH was investigated, revealing the structural modifications and the formation of functional groups. The detailed procedure for synthesizing GQDs using a hydrothermal cleavage approach provides a comprehensive understanding of the formation process. The synthesis parameters, including temperature, reaction time, and composition concentration ratio, were reported to achieve the controlled formation of GQDs. The resulting GQDs were intended for future applications in sensing, particularly for detecting heavy metal ions.

Therefore, we aim to demonstrate the capability of NaOH capability solely, offering a clearer understanding of its impact on fragmentation GO into GQDs formation while contributing to the enhanced optical performance of GQDs through the attachment of functional groups such as hydroxyl and carboxyl groups to optimize the GQDs surface reactivity and chemically stabilize their structure.

2. MATERIALS AND METHODS

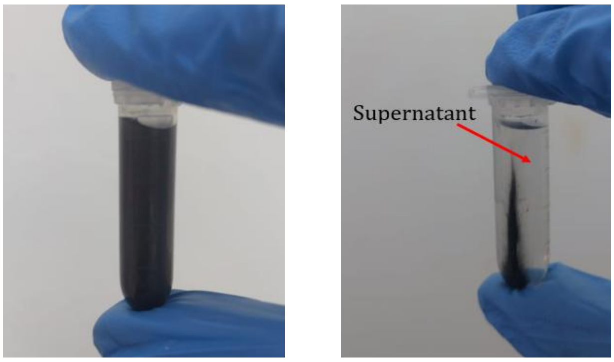
2.1. Materials

The primary precursor material used was the commercially available graphene oxide powder (GO, 15–20 sheets, 4–10% edge oxidized, 796034, 1 g) purchased from Sigma-Aldrich, which served as a basis for the graphene-based framework. The physical characteristic of the GO is in the form of powder with a very dark brown to black color. While the GO chemical profile of > 50.0% carbon, < 5.0% water, and < 11.0% oxygen content. 15–20 sheets suggest a multi-layer GO material, which refers to the number of graphene layers stacked and overlaid on one another. These typical GO thin layers have been chemically oxidized. The 4–10% edge oxidized in the graphene sheets holds an oxygen-containing functional group bonded to approximately 0.04 to 0.10 molar ratio of oxygen to carbon at the sheet edges. The range of edge oxidized enables chemical reactivity by introducing chemical modification while preserving the graphene's structural stability. The synthesis procedure uses sodium hydroxide (NaOH, reagent grade, 97% purity, powder, 655104, 25 g) as a base catalyst. All the chemical components are used without additional purification methods—the experimental procedures used deionized water to maintain the highest purity standards.

2.2. Synthesis of Graphene Quantum Dots

The GQDs were synthesized using hydrothermal cutting approaches according to Mukherjee D. et al. (2022) [12] and Qu et al. (2016) [19] with some modifications. 0.05 g of GO powder was dissolved in 100 mL deionized (DI) water and stirred gently for 15 minutes. The concentration of GO was then treated by sonication for 1 hour to exfoliate the staked GO sheets. 0.1 M NaOH solution was prepared and mixed into GO solution after being cooled at an ambient temperature with a ratio of 1:10. The mixing solution was placed in a 100 mL Teflon-lined autoclave and reacted at 200 °C for 24 hours to facilitate the fragmentation and restructuring GO sheets into GQDs. After cooling to room temperature, the reaction mixture was purified using centrifugation at 8000 rpm for 30 minutes. After centrifugation, the suspension was collected from the supernatant, as shown in Figure 1.

The collected GQD suspension was followed by filtration through 0.22 μm filter paper to achieve nanometer size and subjected to the dialysis process leaves overnight using 1 kDa molecular weight cut-off dialysis to eliminate any remaining sodium ions. Figure 2 illustrates the schematic preparation for synthesizing of GQDs from the hydrothermal cutting.



(a) (b)

Figure 1. (a) Before: GQDs suspension after the hydrothermal cutting process, (b) After: GQDs suspension from the collected supernatant after the centrifugation process.

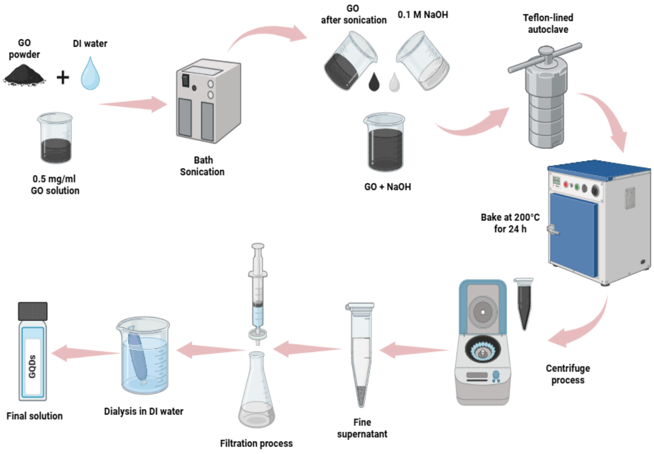


Figure 2. Schematic illustration for synthesizing GQDs from hydrothermal cutting approaches. (Created in Biorender.com)

2.3. Characterization

The synthesized GQDs were characterized on the spectrometer optical analysis, and UV-visible absorption spectra of the GQDs solution were recorded using a Jasco/V-670 EX. The structure of graphitic and defects of the synthesized GQDs were analyzed by Raman Spectroscopy Peek Seeker Agiltron PKR-786 system using a 785-nm excitation laser. The surface functional groups of GQDs were analyzed using Fourier transform infrared (FT-IR) Perkin Elmer Spectrum 400 spectroscopy, and an X-ray diffraction (XRD) pattern was obtained from Rigaku Model Ultima IV. The Ultra-High Resolution (UHR-SEM) images were obtained for morphological analysis using Hitachi Regulus 8220 and Energy-dispersive X-ray (EDX) to identify the elemental composition. The size and morphology of individual GQDs were characterized using Transmission Electron Microscopy (TEM) images obtained on a Zeiss Libra 120. To explore the optical emission characteristics of GQDs, the photoluminescence (PL) spectra were recorded using a MiniPL-5.0 spectrometer. The Zeta Potential Malvern Master Sizer 2000 was utilized to perform dynamic light scattering (DLS) measurement on GQD colloids in solutions to determine particle size distribution, thus providing information on the stability and dispersion characteristics of GQD particles.

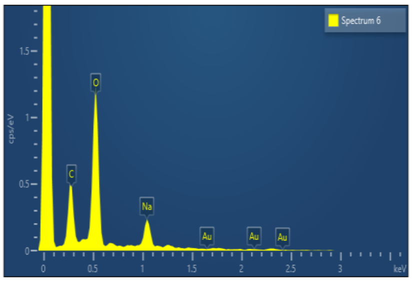
3. RESULT AND DISCUSSION

The hydrothermal method explored a commercial starting material, graphene oxide, in an alkali sodium hydroxide medium to synthesize graphene quantum dots. The synergistic interaction between GO and NaOH was thoroughly investigated, revealing structural modifications and the formation of functional groups. This approach also provides observations on the cutting mechanism and the surface functionalization of the GQDs results.

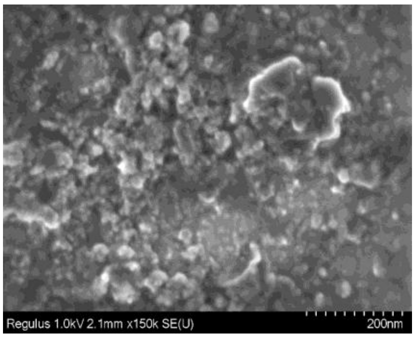
3.1. Surface Morphology Analysis

Figure 3 exhibits the surface morphology analysis of synthesized GQDs. The UHR-SEM is applied to inspect the surface topography of the synthesized GQDs. A spin-coated method was applied to drop a GQDs solution on the gold thin film (AuTF) of 50 nm thickness and bake for 5 minutes at 100 °C. Each step was repeated twice to ensure the solution adhered to the surface of AuTF. The AuTF provides a more stable substrate to enhance imaging consistency. Since glass is an insulator that can accumulate charge under the electron beam, this induces image distortion [20] in the UHR-SEM. Meanwhile, the conductive gold can directly reduce charge accumulation and absorb the excess, leading to more stable and explicit images, particularly in ultrahigh resolution. Therefore, the presence of Au in the EDX spectrum, as in Figure 3(a), is expected. The intense peak at 0 – 0.1 keV in the EDX spectrum is observed due to the influence of background noise or system artifacts found in low-energy ranges, which are typically unrelated to elemental composition.

The synthesized GQDs were formed, as shown in Figure 3(b). The images of GQDs show particles of various sizes in the prepared samples. The results reveal inconsistency in size distributions and form a cluster that resembles a rosette-GQDs. This attributed to multiple justifications: 1) Agglomeration happened, suggesting that the second layer of dropped GQDs solution leads to an increase in the thickness and density of the film; 2) irregular shapes of synthesized GQDs due to NaOH concentration not sufficiently shape and induce fragmentation during the hydrothermal process, suggesting the higher NaOH concentration essentially to implement; and 3) the reported ratio of GO: NaOH amount affect the particle size distribution.



(a)



(b)

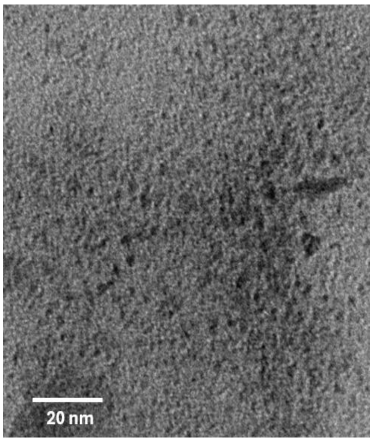
Figure 3. (a) EDX spectrum, (b) UHR SEM image at 200 nm scale bar for GQDs

Figure 3(a) shows the compositional elements of the sample determined using the EDX technique. The compositional elements consisting of C, O, Na and Au in the GQDs sample were tabulated as in Table 1.

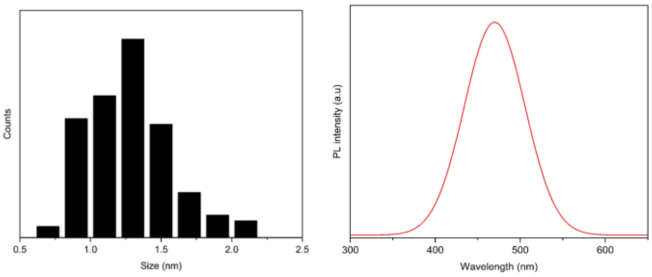
Table 1. The element composition of the synthesized GQDs

Element	Wt %
Carbon (C)	27.83
Oxygen (O)	52.82
Sodium (Na)	19.35
Gold (Au)	0

No unexpected peaks in the visible spectrum indicated no other contaminations from the synthesis process. The presence of a carbon peak has been expected in the composition of GQDs, and the higher peak of oxygen-containing functional groups of 52.82 wt% suggests the successful oxidation process of GO into GQDs, which is comparable to earlier reports [12]. A work report by Nxele S. R. and Nyokong T. (2022) observed that the peak of an oxygen element started to dominate the carbon element for a longer reaction time [21]. The slightly weaker peak of Na obtained is due to the proportion ratio attributed to using the NaOH solution as a shaping process in GQDs.



(a)



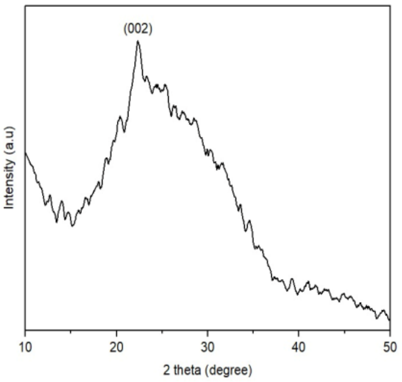
(b) (c)

Figure 4. (a) TEM image, (b) Size distribution, (c) PL spectra of the GQDs.

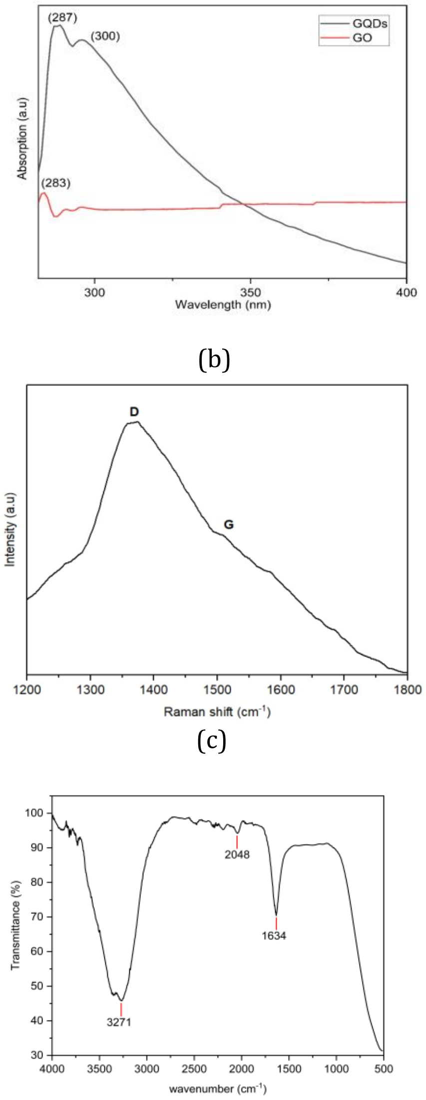
A few drops of GQD solution are dropped on the glass substrate for TEM analysis, as in Figure 4(a), to determine the particle size of GQDs. The analysis reveals an area in TEM grids that emerges the dark cavitating of individual little dots in an irregular shape in minimal size, approximately ~1.3 nm on average, as observed in Figure 4(b). The result exhibits the graphene identify structure, GQDs, which is successfully synthesized by the NaOH. Under low carbonization and the GQDs size of 1.1 - 1.3 nm, the PL spectra of the GQDs were, noticed at 470 nm developed in Figure 4(c), revealing the obvious fluorescent emission.

3.2. Structural and Optical Properties

The alkaline environment condition initiated the exfoliation of GO to produce GQDs. The synthesis of the GQDs via one-step hydrothermal cutting was recorded using several characterization techniques, as shown in Figure 3. The structural analysis of X-ray analysis yielded the formation of GQDs, as shown in Figure 5 (a). The XRD pattern of GQDs shows a broad peak centered at 2θ = 23°, corresponding to the (002) plane, which indicates the disorder graphitic nature of the GQDs in agreement with Raj S. K. et al. (2019) [22]. The widening peak suggested that the ordered structure of the precursor had been modified to form an amorphous structure [23]. The result indicated that the synthesis parameters demonstrated an effective range to prepare GQDs on GO, with the GQDs being fragmented.



(a)



(b)

(c)

(d)

Figure 5. (a) XRD pattern, (b) UV-vis spectrum, (c) Raman spectrum, (d) FTIR spectrum of the GQDs.

The optical properties of UV-visible absorption spectra clearly show distinct features of GO, indicating the transformation of synthesized GQDs. The UV–vis spectrum shown in Figure 5(b) reveals a slight red-shifted from GO (283 nm) to GQDs (287 nm), which seems associated with the π-π* of the aromatic sp2 transition C═C bonds. The shift suggests a quantum confinement effect as a result of size reduction. An extra shoulder peak in synthesized GQDs (300 nm) attributed to the n-π* transition of C═O bonds. This is satisfactory, as previously stated by Saleem H. et al. (2023) [24]. The additional peak supports the emergence of new edge states or functional groups during the quantum dot formation.

The structural properties of the GQDs analyses by the Raman spectra show a broad D band at 1360 cm^{-1} and a diminished peak G band at 1520 cm^{-1}, as illustrated in Figure 5(c). This is comparable to the prior study by Pan D. et al. (2012), which showed the weak peak of the G band with the relatively high-intensity ratio D/G [25]. The D band indicates the disordered carbon structures, while the G band reveals the crystallinity, suggesting GQDs have more defects, edges, and vacancies in the carbon lattice. It has been supported by the previous study reported by Gu J. et al. (2014), who proposed that the higher fluorescence quantum yield disrupts the Raman analysis of the GQDs [26]. The D to G intensity ratio (I_D/I_G) for the synthesized GQDs is 1.54. The result suggests the high density of defects capped with the abundance of oxygenated groups in the GQDs surfaces. The high ratio of the D band to the G band in Raman spectra indicates the highly fragmented nanoscale structures, as smaller graphene fragments contain more edge states consistent with the XRD patterns. An amorphous structure of GQDs indicates the random arrangement of carbon atoms, while the repeating patterns in crystalline graphite contribute to a highly structural disorder.

As shown in Figure 5(d), the FTIR spectra analysis indicated stretching vibration of the functional group in GQDs material. The observed peak at 3271 cm^{-1} is associated with the vibrations of O—H stretching (hydrogen-bonded hydroxyl group), the unusual stretching vibration of 2048 cm^{-1} could correspond to alkyne functional groups during the chemical reactions involving NaOH, and 1634 cm^{-1} are associated with an aromatic strong peak C═C or C═O (carbonyl groups) stretching bonds, respectively. The spectrum reveals the significant presence of hydroxyl groups and oxygenated carbon groups on the surface edge sites of the GQDs enhancing the hydrophilicity and reactivity. More oxygen-containing functional groups indicate the increment in the oxygen content in synthesized GQDs. These functional groups provide good dispersion in water and active binding sites improving the chemical reaction and fluorescence enhancement as reported in [22] and [27]. The oxygen functional groups on the surface of GQDs contribute to the strong interaction with metal ions [23], [28]. Therefore, more oxygen functional groups provide more binding resulting in better detection.

Figure 6 shows the zeta potential, ζ of the synthesized GQDs recorded in solution. The zeta potential is associated with the stability of dispersions. The chemical functionalization of GQDs is one of the decisive factors influencing the stability of solutions. The GQDs reveal a negatively charged particle value of -19.1 mV, indicating the satisfactory stability level of conjugates in dispersion form. It can be said that the higher the +/- zeta potential, the larger the electrostatic repulsion between the particles. The result is also supported by [29], which found that the ζ of GQDs (-15.5 mV) showed a negative surface charge with acceptable stability. The observed GQDs also have a lower polydispersity index (PDI) value of 0.486, as reported in Figure 7, indicating average dispersity, which both criteria ensure robustness and suitability for long-term applications.

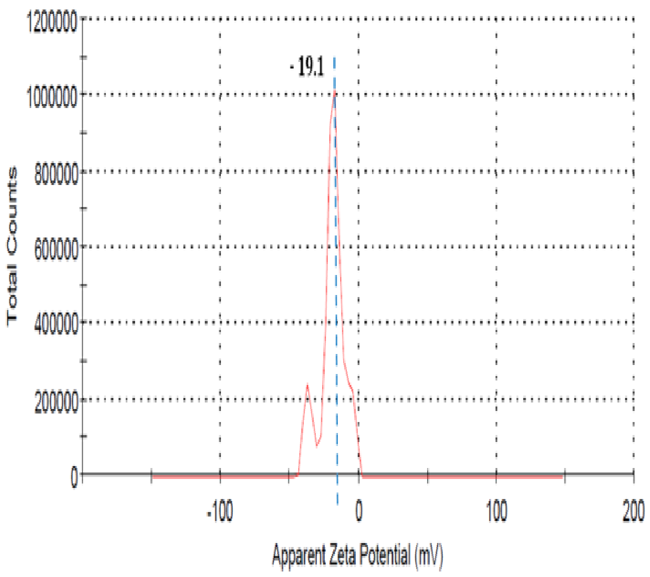
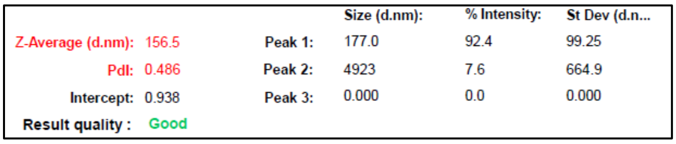


Figure 6. Zeta potential, ζ graph for synthesized GQDs



			Size (d.nm):	% Intensity:	St Dev (d.n...
Z-Average (d.nm):	156.5	Peak 1:	177.0	92.4	99.25
PdI:	0.486	Peak 2:	4923	7.6	664.9
Intercept:	0.938	Peak 3:	0.000	0.0	0.000
Result quality :	Good				

Figure 7. Polydispersity index (PDI) of the GQDs

Table 2 compares of several methods for synthesized GQDs employing different additives and challenges. Hydrothermal cutting after NaOH as an additive poses several advantages and is an attractive approach for GQD formation. Besides its simplicity, safety, and reduced environmental impact, this method offers a more straightforward alternative, unlike methods that require harsh chemicals such as HNO_3, $KMnO_4$ and H_2O_2. This method infuses confidence in the method application. Despite that, achieving uniform size in GQDs and sustaining optimal properties still require thorough control of reaction conditions, especially the NaOH concentration and the hydrothermal parameters.

Table 2. Comparison analysis of GQDs synthesis methods, precursors/additives and challenges.

Method	Precursors/Additives	Challenges	Study
Sonochemistry & microwave	GO, $KMnO_4$	Uses strong oxidants and handling safety concerns.	[30]
Alkaline Thermal treatment	Crude GO, KOH	Required careful controlled heat and solid-solid phase reactions can limit size uniformity.	[31]
Chemical oxidation	Vulcan XC-72 carbon black, HNO_3	Uses strong acids (HNO_3), corrosive waster and complex separation.	[32]
Hydrothemal etching	HNO_3	Relies on strong acid (HNO_3) as an oxidant for dopant and required purification steps.	[33]
Solvothermal	GO, H_2O_2, DMF	Uses hydrogen peroxide (H_2O_2), and organic solvent (DMF); a multi-step control needed and relatively long time.	[34]
Hydrothermal cutting	Commercial GO (edge-oxidized), NaOH	Sodium hydroxide (NaOH) cleavage as a single element and dopant-free synthesis	This work

3.3 Synergistic Effect of Graphene Oxide and Sodium Hydroxide

GQDs were prepared in the presence of GO and NaOH in the hydrothermal cutting process. The system is divided into three principal stages: 1) pre-treatment, 2) the hydrothermal reaction, and 3) post-reaction. The pre-treatment process starts with NaOH before the hydrothermal reaction procedures activate the oxygen functional groups on GO. This process is a deprotonation reaction where NaOH reacts with the acidic groups (-COOH and -OH) on the GO surface. A strong base removes a portion (H^+) from them to neutralize the acidic group, which makes it easier to fragment the GO. The loosened GO was heated at high temperatures and pressures through hydrothermal cutting. During the process, the NaOH operates in two ways: i) the alkaline medium base breaks the epoxy bonds such as C-O-C in GO by adding water molecules[35], [36], and ii) initiates reactive oxygen radicals that cut the carbon network [35], [36]. At this point, the combined heat and NaOH weaken the GO sheet’s structure, thus creating cracks and defects into tiny fragments of GQDs. The final post-reaction process is a reduction by NaOH reducing agent. NaOH eliminates the -COOH groups by turning them into CO_2 and converts the unstable oxygen groups (C=O) into more stable structures by stabilizing the edge of GQDs to avoid clumping together [37]. However, despite removing some oxygen, the total oxygen content increases because of new edges created during cutting and oxidized by highly reactive molecules derived from oxygen, besides the sodium ions (Na^+) sticking to the edges, contributing to the higher oxygen appearance in the sample.

Generally, GO has rich oxygen-containing functional groups and hydrophilic groups that enhance its hydrophilicity. While NaOH is a strong base, it displays significant advantages in this synthesis process. It reacts with GO under heat to produce unstable bonds. The alkaline base also facilitates the oxidative cutting of GO into smaller fragments and new edges, which is crucial for the formation of GQDs.

In the process of the hydrothermal reaction system, the synergistic effect of NaOH, combined with the oxygen functional group on GO, can lead to chemical reactions breaking down the GO into smaller fragments, inducing stretching, distortion, and cleavage of the GO sheets due to localized chemical and thermal stresses during the hydrothermal cutting process. As a result, the NaOH helps the carbonization process for carbon oxidation. Various functional groups, such as hydroxyl, carbonyl, or carboxyl groups, are generated or modified on the surface. The chemical reaction reorganized these tiny fragments into GQDs and enhanced the surface chemical states, curvature, and edge effects which contribute to the defect structure in GQDs and increment in the oxygen proportion.

Overall, the GO and NaOH can work together as a team. Each lead to the formation of GQDs as tiny and fluorescent nanoparticles. As the NaOH loosens the GO sheets layers, they become fragile. The given heat and the highly reactive molecules cut the layers, and finally, NaOH polishes the tiny pieces called GQDs.

4. CONCLUSION

This study demonstrated the one-step hydrothermal cutting method for synthesizing GQDs, leveraging commercially available GO precursor, and the oxidation reaction from an alkaline base NaOH, highlights the synergistic effect of both reagents. The environmentally sustainable and cost-effective optimized approach avoids harsh chemicals and sets an optimal standard for GQDs with tuneable structural and optical properties.

The 4–10% edge oxidized graphene oxide reacted well with the oxidizing agent, NaOH, yielding successful results for the synthesized GQDs. NaOH induces deprotonation of oxygen-functional groups in GO, thus enabling the structural fragmentation and resulting formation of nanoscale GQDs. However, the concentration of NaOH, by implication, elevated the degree of oxidation in the GQDs material, which indicate the degradation of the graphitic structure of the GQDs due to carbon loss during oxidative degradation and the dominance of cutting over reduction promotes excessive fragmentation.

The characterization verified the attainment synthesizes of GQDs with several important aspects, including structural stability, optical properties, and surface functionalization The outcomes demonstrate the successful synthesis of advanced GQDs with fair structural, optical, and chemical properties. The high degree of crystalline obtained by the broad peak in XRD and the high I_D/I_G ratio, Raman spectroscopy confirms the presence of quantum confinement and edge effects. The UV-Vis and FTIR support optical properties, indicating the electronic transitions and identifying the chemical functional groups. The analyzed zeta potential associated with the stability of dispersions found that the GQDs are stable in the solution due to the negatively charged surface. The UHR-SEM, TEM, and EDX confirm the structural morphology and element composition of GQDs, indicating the success of the synthesized GQDs.

The interaction between GO and NaOH promotes the involvement of oxygen functional groups in the carbon surface, motivating the formation mechanism of GQDs. For specific applications such as sensing implementation, the higher oxygen-containing functional group improves the chemical reactivity or adsorption ability more effectively, unveiling new potential for improving GQDs research. The reduction process can be developed further by managing the concentration ratio GO:NaOH during synthesis. GQDs from the interaction between GO and NaOH further investigate using different GO and NaOH concentrations solutions to observe the graphitic structure element and the introduction of increased oxygen functional group in GQDs.

This study aims to design reliable and sensitive sensing for heavy metal detection. Therefore, in the subsequent studies, the long-term stability assessments of the synthesize GQDs under various environmental conditions are required to be conducted to evaluate the robustness of GQDs for real-world applications.

ACKNOWLEDGMENTS

This research was made possible with MOHE funded the project through the Fundamental Research Grant Scheme (FRGS) (FRGS/1/2023/TK07/UITM/02/26) enabling the procurement of materials and access to advanced characterization equipment and the generous support of Universiti Teknologi MARA (UiTM).

REFERENCES

[1] S. A. I. Sheikh Mohd Ghazali, I. Fatimah, Z. N. Zamil, N. N. Zulkifli, and N. Adam, "Graphene quantum dots: A comprehensive overview," Jan. 01, 2023, *De Gruyter Open Ltd*. doi: 10.1515/chem-2022-0285.

[2] X. Zhu *et al.*, "Recent Advances of Graphene Quantum Dots in Chemiresistive Gas Sensors," Nov. 01, 2023, *Multidisciplinary Digital Publishing Institute (MDPI)*. doi: 10.3390/nano13212880.

[3] S. A. Ansari, "Graphene Quantum Dots: Novel Properties and Their Applications for Energy Storage Devices," Nov. 01, 2022, *MDPI*. doi: 10.3390/nano12213814.

[4] H. Shin, M. Y. Lim, J. Oh, Y. Lee, and J. C. Lee, "Preparation of bottom-up graphene oxide using citric acid and tannic acid, and its application as a filler for polypropylene nanocomposites," *RSC Adv*, vol. 11, no. 13, pp. 7663–7671, Feb. 2021, doi: 10.1039/d0ra09856f.

[5] R. Liu, D. Wu, X. Feng, and K. Müllen, "Bottom-up fabrication of photoluminescent graphene quantum dots with uniform morphology," *J Am Chem Soc*, vol. 133, no. 39, pp. 15221–15223, Oct. 2011, doi: 10.1021/ja204953k.

[6] E. Suvaci and E. Özel, "Hydrothermal Synthesis," in *Encyclopedia of Materials: Technical Ceramics and Glasses: Volume 1-3*, vol. 1, Elsevier, 2021, pp. V1-59-V1-68. doi: 10.1016/B978-0-12-803581-8.12096-X.

[7] T. Yusaf *et al.*, "A Comprehensive Review on Graphene Nanoparticles: Preparation, Properties, and Applications," *Sustainability (Switzerland)*, vol. 14, no. 12336, Oct. 2022, doi: 10.3390/su141912336.

[8] R. T. M. Ahmad, S. H. Hong, T. Z. Shen, and J. K. Song, "Water-assisted stable dispersal of graphene oxide in non-dispersible solvents and skin formation on the GO dispersion," *Carbon N Y*, vol. 98, pp. 188–194, Mar. 2016, doi: 10.1016/j.carbon.2015.11.007.

[9] F. Mouhat, F. X. Coudert, and M. L. Bocquet, "Structure and chemistry of graphene oxide in liquid water from first principles," *Nat Commun*, vol. 11, no. 1, Dec. 2020, doi: 10.1038/s41467-020-15381-y.

[10] Y. Huang *et al.*, "Advances in synthesis of the graphene quantum dots from varied raw materials," *Arabian Journal of Chemistry*, vol. 17, no. 2, Feb. 2024, doi: 10.1016/j.arabjc.2023.105533.

[11] M. H. M. Facure, R. Schneider, L. A. Mercante, and D. S. Correa, "Rational hydrothermal synthesis of graphene quantum dots with optimized luminescent properties for sensing applications," *Mater Today Chem*, vol. 23, Mar. 2022, doi: 10.1016/j.mtchem.2021.100755.

[12] D. Mukherjee, P. Das, S. Kundu, and B. Mandal, "Engineering of graphene quantum dots by varying the properties of graphene oxide for fluorescence detection of picric acid," *Chemosphere*, vol. 300, Aug. 2022, doi: 10.1016/j.chemosphere.2022.134432.

[13] D. Pan, J. Zhang, Z. Li, and M. Wu, "Hydrothermal route for cutting graphene sheets into blue-luminescent graphene quantum dots," *Advanced Materials*, vol. 22, no. 6, pp. 734–738, Feb. 2010, doi: 10.1002/adma.200902825.

[14] B. Anegbe, I. H. Ifijen, M. Maliki, I. E. Uwidia, and A. I. Aigbodion, "Graphene oxide synthesis and applications in emerging contaminant removal: a comprehensive review," *Environ Sci Eur*, vol. 36, no. 15, Dec. 2024, doi: 10.1186/s12302-023-00814-4.

[15] P. Zare, M. Aleemardani, A. Seifalian, Z. Bagher, and A. M. Seifalian, "Graphene oxide: Opportunities and Challenges in Biomedicine," *Nanomaterials*, vol. 11, no. 5, May 2021, doi: 10.3390/nano11051083.

[16] M. Velický, P. S. Toth, C. R. Woods, K. S. Novoselov, and R. A. W. Dryfe, "Electrochemistry of the Basal Plane versus Edge Plane of Graphite Revisited," *Journal of Physical Chemistry C*, vol. 123, no. 18, pp. 11677–11685, May 2019, doi: 10.1021/acs.jpcc.9b01010.

[17] X. Xiao, Y. Zhang, L. Zhou, B. Li, and L. Gu, "Photoluminescence and Fluorescence Quenching of Graphene Oxide: A Review," *Nanomaterials*, vol. 12, no. 14, Jul. 2022, doi: 10.3390/nano12142444.

[18] W. Chen, G. Lv, W. Hu, D. Li, S. Chen, and Z. Dai, "Synthesis and applications of graphene quantum dots: A review," Apr. 25, 2018, *Walter de Gruyter GmbH*. doi: 10.1515/ntrev-2017-0199.

[19] A. Qu, H. Xie, X. Xu, Y. Zhang, S. Wen, and Y. Cui, "High quantum yield graphene quantum dots decorated TiO2 nanotubes for enhancing photocatalytic activity," *Appl Surf Sci*, vol. 375, pp. 230–241, Jul. 2016, doi: 10.1016/j.apsusc.2016.03.077.

[20] R. FlatabØ, A. Coste, and M. M. Greve, "A systematic investigation of the charging effect in scanning electron microscopy for metal nanostructures on insulating substrates," *J Microsc*, vol. 265, no. 3, pp. 287–297, Mar. 2016, doi: 10.1111/jmi.12497.

[21] S. R. Nxele and T. Nyokong, "Time-dependent characterization of graphene quantum dots and graphitic carbon nitride quantum dots synthesized by hydrothermal methods," *Diam Relat Mater*, vol. 121, Jan. 2022, doi: 10.1016/j.diamond.2021.108751.

[22] S. K. Raj, V. Yadav, G. R. Bhadu, R. Patidar, M. Kumar, and V. Kulshrestha, "Synthesis of highly fluorescent and water soluble graphene quantum dots for detection of heavy metal ions in aqueous media," *Environmental Science and Pollution Research*, vol. 28, no. 34, pp. 46336–46342, Sep. 2020, doi: 10.1007/s11356-020-07891-5.

[23] A. Saud, H. Saleem, N. Munira, A. A. Shahab, H. Rahman Siddiqui, and S. J. Zaidi, "Sustainable Preparation of Graphene Quantum Dots for Metal Ion Sensing Application," *Nanomaterials*, vol. 13, no. 1, Jan. 2023, doi: 10.3390/nano13010148.

[24] H. Saleem, A. Saud, and S. J. Zaidi, "Sustainable Preparation of Graphene Quantum Dots from Leaves of Date Palm Tree," *ACS Omega*, vol. 8, no. 31, pp. 28098–28108, Aug. 2023, doi: 10.1021/acsomega.3c00694.

[25] D. Pan *et al.*, "Cutting sp2 clusters in graphene sheets into colloidal graphene quantum dots with strong green fluorescence," *J Mater Chem*, vol. 22, no. 8, pp. 3314–3318, Feb. 2012, doi: 10.1039/c2jm16005f.

[26] J. Gu, M. J. Hu, Q. Q. Guo, Z. F. Ding, X. L. Sun, and J. Yang, "High-yield synthesis of Graphene Quantum Dots with Strong Green Photoluminescence," *RSC Adv*, vol. 4, no. 91, 2014, doi: 10.1039/c4ra10011e.

[27] M. S. Al Ja'farawy *et al.*, "Graphene quantum dot nanocomposites: electroanalytical and optical sensor technology perspective," *J Anal Sci Technol*, vol. 14, no. 1, Dec. 2023, doi: 10.1186/s40543-023-00393-2.

[28] Y. L. Zhang *et al.*, "Graphitic carbon quantum dots as a fluorescent sensing platform for highly efficient detection of Fe3+ ions," *RSC Adv*, vol. 3, no. 11, pp. 3733–3738, Mar. 2013, doi: 10.1039/c3ra23410j.

[29] W. Saeed, Z. Abbasi, M. Bilal, S. H. Shah, A. Waseem, and A. J. Shaikh, "Interactive behavior of graphene quantum dots towards noble metal surfaces," *Physica E Low Dimens Syst Nanostruct*, vol. 147, Mar. 2023, doi: 10.1016/j.physe.2022.115596.

[30] R. V. Nair, R. T. Thomas, V. Sankar, H. Muhammad, M. Dong, and S. Pillai, "Rapid, Acid-Free Synthesis of High-Quality Graphene Quantum Dots for

Aggregation Induced Sensing of Metal Ions and Bioimaging," *ACS Omega*, vol. 2, no. 11, pp. 8051–8061, Nov. 2017, doi: 10.1021/acsomega.7b01262.

[31] S. Yang *et al.*, "A novel synthesis of graphene quantum dots via thermal treatment of crude graphite oxide in a dry and alkaline condition, and their application in uranyl detection," *Heliyon*, vol. 6, no. 9, Sep. 2020, doi: 10.1016/j.heliyon.2020.e04533.

[32] F. Liu *et al.*, "Gram-scale synthesis of high-purity graphene quantum dots with multicolor photoluminescence," *RSC Adv*, vol. 5, no. 126, pp. 103428–103432, 2015, doi: 10.1039/C5RA19219F.

[33] M. Zhao, "Direct synthesis of graphene quantum dots with different fluorescence properties by oxidation of graphene oxide using nitric acid," *Applied Sciences (Switzerland)*, vol. 8, no. 8, Aug. 2018, doi: 10.3390/app8081303.

[34] C. Carrera, A. Galán-González, W. K. Maser, and A. M. Benito, "Multifaceted role of H2O2 in the solvothermal synthesis of green-emitting nitrogen-doped graphene quantum dots," *Chem Sci*, no. 16, pp. 3662–3670, Jan. 2025, doi: 10.1039/d4sc07896a.

[35] C. Chen, W. Kong, H. M. Duan, and J. Zhang, "Theoretical simulation of reduction mechanism of graphene oxide in sodium hydroxide solution," *Physical Chemistry Chemical Physics*, vol. 16, no. 25, pp. 12858–12864, Jul. 2014, doi: 10.1039/c4cp01031k.

[36] J. Ärnström and L. Altalouli, "Chemical reduction of graphene oxide using different reducing agents Chemical Reduction," 2020.

[37] L. Zhao, Y. Wang, and Y. Li, "Antioxidant activity of graphene quantum dots prepared in different electrolyte environments," *Nanomaterials*, vol. 9, no. 12, Dec. 2019, doi: 10.3390/nano9121708.