

Facile One-Step Preparation and Characterization of Graphene Quantum Dots Suspension via Electrochemical Exfoliation

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This study reports on the production of graphene quantum dots (GQDs) suspension using a simple electrochemical setup which involved an electrolyte solution, consisting of citric acid and sodium hydroxide (NaOH) mixture, and pristine graphite rods for the electrode without any heating treatment (calcination), thus avoiding any high energy consumption. The balanced reaction mixture of citric acid and NaOH was used to investigate the effects of reaction time and voltage used towards the production of GQDs. UV-Vis spectroscopy analysis revealed significant UV absorption around 240-255 nm which depicted $\pi \rightarrow \pi^*$ transition of aromatic sp^2 C-C bonds while FTIR analysis showed the significant C=C stretching band around 1635 cm^{-1} attributed by the aromatic ring. The exfoliation of the GQDs was increased as the concentration of NaOH in the electrolyte, time taken and voltage were increased. The optimum GQDs suspension can be obtained using a balanced ratio of citric acid and NaOH with a voltage of 10 V for 2 hours reaction time. TEM analysis confirmed the presence of the GQDs obtained with an average size of ~5 nm for the optimum GQDs suspension. The exfoliation of GQDs via the electrochemical technique may pave the way towards upscale and sustainable production of the nanomaterial.

Key words: Graphene; graphene quantum dots; suspension; electrochemical; exfoliation

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Since the discovery of graphene by the Nobel winners, Geim and Novoselov [1], scientists, academia, industries and government agencies have been actively involved in exploring graphene, with innumerable number of fundamental, theoretical and experimental studies reported. Graphene, a two-dimensional monolayer of sp^2 bonded carbon atoms that are arranged in hexagonal lattice form [2] is an exceptional and emerging carbon-based nanomaterial with superior properties and versatility. A chopped fragment of graphene sheets is called graphene quantum dots (GQDs) and it represents a zero-dimensional member in the graphene family, with unique features of edge effects and quantum confinement properties [3,4]. GQDs can be synthesized using graphene-based precursors or materials with graphene-like structure including carbon nanotubes (CNTs) and polycyclic aromatic hydrocarbons [5]. Nanoscale size range of graphene is considered as graphene nanoflakes and usually appeared with arbitrary shape and lateral dimension. Much smaller particle derived from the graphene flakes produce a quasi-zero-dimensional nanostructures, known as GQDs [5].

In the last few years, extensive efforts had been devoted to investigate the properties and strategy of preparing high-quality and monodisperse GQDs. The strategies for the preparation of GQDs fall into two major categories, which are the top-down and bottom-up approach. The top-down approach refers to GQDs that are obtained using precursors of graphite, graphene or graphene-like structure materials. In other words, it involves the exfoliation of the raw bulk material or graphitic materials into GQDs, thus the GQDs produced will be high graphitic in nature. Some reported literatures under this category of top-down procedure include hydrothermal (chemical) cutting [6], acid treatment and chemical exfoliation [7], microwave irradiation [8] and electrochemical exfoliation [9]. These top-down approaches usually resulted in a high density of functional groups at the edges as the methods involved the fragmentation through a chemical oxidation-reduction process and the solubility of the GQDs favoured due to the functional groups present. The latter category (bottom-up strategy) of GQDs synthesis is through a step-wise chemical synthesis using a molecular precursor. Some examples of the bottom-up synthesis

of the GQDs are citric acid pyrolysis [10], substituted benzene derivatives precursor oxidation and stepwise solution chemistry [11], fragmentations of fullerenes [12] and others. Despite the fact that the bottom-up approach requires a more challenging step-wise chemical synthesis from a molecular precursor with rigorous experimental conditions, this approach offers a better control of shape and size of the GQDs.

The tremendous interest in GQDs by the scientific communities and its remarkable properties and unique structures, has interested us to explore GQDs fundamentally, including its eco-friendly preparation. To avoid a rigorous experimental condition and a challenging step-wise chemical synthesis, a facile top-down preparation was adopted in this work. The GQDs was produced using an electrochemical technique with ion-intercalation and exfoliation mechanisms. Top-down approaches are simpler, more efficient and affordable as compared to bottom-up which require special equipment and are time-consuming. Hence, in this study, top-down approach was chosen to prepare the GQDs, by using electrochemical exfoliation of graphite rod. Several works have been reported on the electrochemical exfoliation of graphite into GQDs using various electrolyte precursors such as potassium persulfate [13], sodium methoxide [14], sodium phytate [15] and, sodium hydroxide and semicarbazide mixture [9]. In this work, the mixture of sodium hydroxide and citric acid was used as the electrolyte for the electrochemical exfoliation of GQDs, similar to previous work by Ahirwar *et al.* [16], except that the electrode was used without any heating treatment (calcination) to avoid any high energy consumption in order to promote and ensure sustainable production of the nanomaterial. It is expected that the formation of citrate ions in the electrolyte, would be sufficient and responsible for an efficient production of the GQDs. This can hopefully be achieved via

active ions interaction and intercalation with the graphite electrode due to the presence of multiple anionic oxygen moieties in the citrate molecule as compared to other electrolyte precursors. A schematic diagram of the electrochemical exfoliation process is illustrated in Figure 1. Among the advantages of electro-chemistry are that it is a simple, economic and non-hazardous method compared to the chemical oxidation method which also suffers from a complicated washing procedure. The effects of concentration of the electrolytes and electrochemical reaction time on the prepared GQDs were also investigated. The synthesized GQDs were characterized using transmission electron microscopy (TEM), attenuated total reflection Fourier transform infrared spectrometry (FTIR), and UV-Vis spectroscopy.

MATERIALS AND METHODS

Materials

All the chemicals in this research were used without any pre-treatment. Sodium hydroxide (NaOH) and citric acid ($C_6H_8O_7$) were supplied by Merck and Sigma-Aldrich respectively. Graphite rods were purchased from Yinxuan Carbon while the DC power supply was purchased from Hitechrons Sdn. Bhd.

Electrochemical preparation of GQDs

The electrochemical exfoliation of graphite method involved the use of a simple two-electrode system using a DC power supply, two graphite rods and an electrolyte solution. The setup for the electrochemical method is as shown in Figure 1. The method used in this work was adapted from Ahirwar and his co-worker [16], except that the electrodes were used without any heating treatment (calcination) to

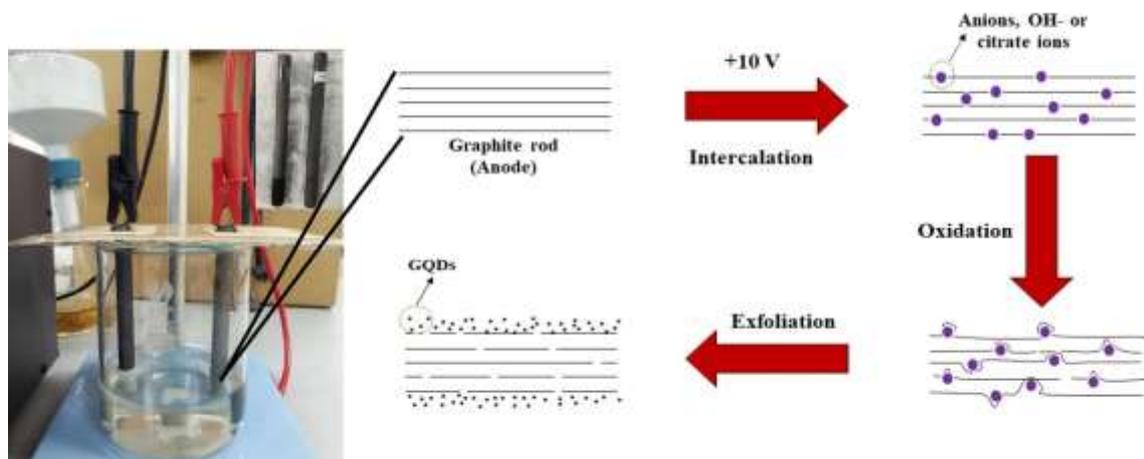


Figure 1. Schematic illustration of electrochemical exfoliation of graphite rod at anode.

introduce surface defects, thus avoiding high energy consumption. The concentration of citric acid was maintained at 0.1 M while the concentration of NaOH was varied to (0.15 M, 0.2 M, 0.3 M and 0.4 M). A 100 ml of electrolyte solution was used with two graphite rods as the electrodes with diameters of 0.8 cm and lengths of 10 cm. The graphite rods were washed with distilled water before used. A constant voltage of 10 V was applied for two hours of electrolysis time. The exfoliation of graphite rod can be observed by the changing of a colourless electrolyte solution to a yellow solution. The experiment was repeated using a mixture of 0.1 M citric acid and 0.3 NaOH under 10 V voltage but with different electrolysis time of 1 hour and 3 hours to investigate the effect of electrolysis time on GQDs production. The experiment was also repeated using different voltages of 8 V and 12 V using the same mixture concentration for 2 hours of electrolysis time. The parameters used in preparing the GQDs are summarized in Table 1. Theoretically, the preparation of GQDs from graphite rod was obtained by the intercalation of anions into the graphite rod, which lead to exfoliation as generally summarized in Figure 1.

Characterization

UV-visible absorption spectra were recorded on a double beam UV-visible spectrophotometer (Perkin Elmer) for all GQDs samples. The functional groups on the GQDs samples were confirmed and analyzed using an attenuated total reflection Fourier transform infrared spectrometer (Perkin Elmer Frontier) at 4000–500 cm^{-1} wavelength. The morphological information of the GQDs were analyzed by Transmission Electron Microscopy (TEM, Zeiss).

RESULTS AND DISCUSSION

From the experimental results, it was observed that a stable GQDs suspension was obtained via the electrochemical process as a result of intercalation of anions onto the graphite electrode (anode) followed by electrochemical exfoliation of the intercalated graphite electrode due to expansion of the Van der Waals spacing of the graphite rod leading to exfoliation. The electrochemical reaction resulted in the colourless electrolyte solution changing to yellow, indicating the successful exfoliation of the graphite in producing GQDs.

Table 1. Parameter used in preparing GQDs.

Sample	Concentration of citric acid:NaOH (M)	Time (H)	Voltage (V)
GQD1	0.1:0.15	2	10
GQD2	0.1:0.2	2	10
GQD3	0.1:0.3	2	10
GQD4	0.1:0.4	2	10
GQD5	0.1:0.3	1	10
GQD6	0.1:0.3	3	10
GQD7	0.1:0.3	2	8
GQD8	0.1:0.3	2	12



Figure 2. Digital image of the GQDs samples produced using various NaOH concentrations (a) GQD1, (b) GQD2, (c) GQD3 and (d) GQD4.

The effect of different electrolyte concentration was investigated by varying the concentration of NaOH in the electrolyte for various formation of anions functional groups. Different concentrations of NaOH in the electrolyte resulted in different concentrations of GQDs as observed by the degree of colour changes shown in Figure 2. The higher the concentration of NaOH used, the darker the resulting solution which marked the increase in exfoliation of the graphite. Both samples of GQD and GQD2 produced yellowish solutions while GQD3 and GQD4 produced brownish solutions (Figure 2). The usage of various NaOH concentrations results in different anion distribution in the electrolyte, thus producing the different exfoliation rate. Sample GQD3 with a ratio of 1:3 citric acid:NaOH is designated as the balanced ratio which resulted in optimal anions intercalation for the formation of GQDs as proposed by Ahiwar *et al.* [16].

Figure 3a shows the comparison of colour changes of the electrolyte after one hour, two hours and three hours of electrochemical reaction. It was observed that the colour became darker as the time was increased. This indicate that the longer the electrolysis time, the higher is the concentration of GQDs produced. Based on this observation, longer electrochemical reaction time may be required to produce higher quantity of GQDs. Based on previous studies [17], the amount of exfoliated product is proportional to the voltage applied. This can also be observed in Figure 3b, which shows the colour of the electrolyte solutions becoming darker from 8 V to 12 V. This showed that increasing the voltage lead to an increase in the production of GQDs exfoliated from the graphite rod. Based on these three parameters, it

can be deduced that increasing the concentration of NaOH in the electrolyte, time taken for the electrolysis process and the voltage applied will increase the production of GQDs. Increasing the time taken and the voltage applied is preferred for the large scale production of GQDs.

UV-vis Spectroscopy

The GQDs samples were characterized using UV-vis spectroscopy for qualitative and quantitative analyses. As shown in Figure 4a, a prominent absorption peak is observed for each GQD1-GQD4 between 240-255 nm which depicts $\pi \rightarrow \pi^*$ transition of the aromatic sp^2 C-C bonds [18]. The $\pi \rightarrow \pi^*$ transition absorption peak of sp^2 C-C aromatic bonds for GQD4 is observed to be broader as compared to that of the others. The broader peak obtained was due to a broader distribution of particle sizes of the GQDs produced [19]. The absorption peaks were also observed to increase from GQD1-GQD4 as the concentration of NaOH in the electrolyte was increased indicating that increasing the concentration of NaOH would result in increasing-the exfoliation of GQDs.

Figure 4b shows the UV-vis spectra of the GQDs produced under different electrochemical reaction time. Similar to the case above, the strong UV absorption between 246-255 nm observed—here can also be attributed to the $\pi \rightarrow \pi^*$ transition of the aromatic sp^2 C-C bond. It was observed that the longer the time taken for the electrochemical exfoliation to occur, the broader are the absorption peaks obtained. Therefore, an increase in electrolysis time will result in the production of a broader range of the particle size distribution, whereby the particles will absorb light at



Figure 3. Digital images of GQDs samples produced (a) under different reaction time of 1 H (GQD5), 2 H (GQD3) and 3 H (GQD6), and (b) under different voltage of 8 V (GQD7), 10 V (GQD3) and 12 V (GQD8).

different wavelengths. However, a prominent shoulder peak at 350 nm was observed for GQD6 which depicts a $n \rightarrow \pi^*$ transition of the C=O bond or other connected groups [18]. The presence of high absorptivity of C=O bond might be due to the longer reaction time which resulted in a higher rate of oxidation. Moreover, the absorbances also increased from one hour to three hours, indicating the increase in concentrations of the GQDs obtained. The prominent shoulder peak of GQD6 at 350 nm which can be ascribed to the transition of C=O bond, showed that the exfoliation of GQDs had reached its optimum reaction at 2 hours. After 2 hours, the peaks showed a significant presence of the C=O bond which can be attributed to the production of graphene oxide quantum dots (GOQDs).

The UV-Vis spectra of GQDs in a 1:3 citric acid:NaOH mixture with three different applied voltages of 8 V, 10 V and 12 V are as shown in Figure 4c. Based on the UV spectra, the prominent absorption peaks were observed to appear between

250-312 nm, attributable to $\pi \rightarrow \pi^*$ transition of the sp^2 aromatic C-C bonds. The GQD7 spectrum showed similar UV absorption as compared to the GQD3. However, the absorption peak of GQD8 was shifted to the right (bathochromic), corresponding to the $n \rightarrow \pi^*$ transition of the C=O. This may be due to the higher degree of oxidation occurring in GQD8 with the higher voltage applied operation, resulting in poorer quality of the spectrum as compared to GQD7 and GQD3. Due to the poor quality of the GQD8 spectrum and its bathochromic shift, it showed that the exfoliation of GQDs in this work had reached its optimum potential at ~ 10 V.

ATR-FTIR Spectroscopy

The functional groups of the GQDs samples were analyzed and confirmed using an attenuated total reflection FTIR spectrometer in the range of 4000-500 cm^{-1} . The FTIR spectra for all the GQDs samples showed similar characteristic absorption bands which

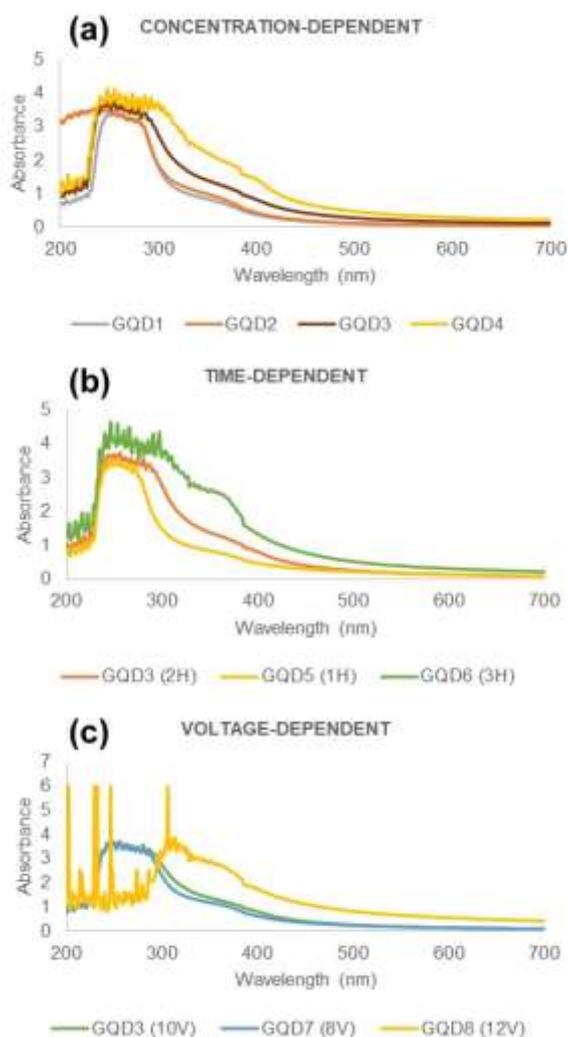


Figure 4. UV-Vis spectra of the GQDs produced using (a) various NaOH concentrations (b) different reaction times, and (c) different voltages.

consisted of the stretching and bending vibration of -OH groups around $\sim 3450\text{ cm}^{-1}$, C=C stretching band at $\sim 1635\text{ cm}^{-1}$, O-H deformation vibration at $\sim 1365\text{ cm}^{-1}$, and phenolic hydroxyl group stretching of the C-OH groups at $\sim 1265\text{ cm}^{-1}$ [20]. Briefly, the FTIR spectra for GQDs prepared from various concentrations of electrolytes as shown in Figure 5a, exhibit absorption bands at $\sim 3320\text{ cm}^{-1}$ corresponding to the stretching and bending vibration of -OH group, C=C stretching at 1635 cm^{-1} , O-H vibration at 1375 cm^{-1} and C-O groups stretching at 1217 cm^{-1} . The GQDs obtained using various electrolyte concentrations give similar spectra except those for GQD1 and GQD2 which exhibit very weak absorption bands at 1375 cm^{-1} and 1217 cm^{-1} as compared to the spectra for GQD3 and GQD4, which are attributed to the O-H vibration and C-O stretching respectively. This may be due to the higher concentrations of NaOH used in the production of GQD3 and GQD4.

The FTIR spectra for GQDs prepared from various reaction times is shown in Figure 5b for GQD3, GQD5 and GQD6 where similar FTIR spectra were observed. These spectra also exhibit absorption bands at 3326 cm^{-1} which corresponds to the stretching and bending vibration of -OH groups and at $\sim 1630\text{ cm}^{-1}$ attributed to the stretching of C=C groups. The band at 1375 cm^{-1} represents O-H bending while the C-O stretching of band was observed at 1217 cm^{-1} . Figure 5c shows the overlaid FTIR spectra for GQD7, GQD3, and GQD8 with different applied voltages of 8 V, 10 V and 12 V respectively. From the FTIR spectra, no significant difference in FTIR absorption bands were observed for GQDs produced under various voltage operations. Similar to GQD3, GQD7 and GQD8 exhibit similar characteristic absorption bands. The obtained FTIR spectra for all GQDs samples indicated the presence of significant C=C stretching groups due to the formation of C=C-C stretch groups (in the aromatic ring) [21].

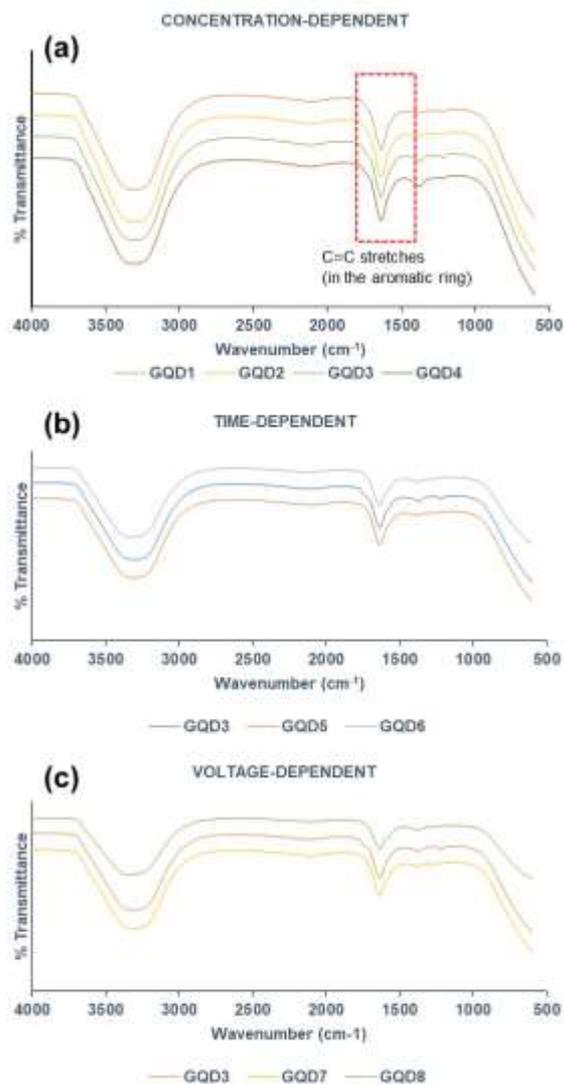


Figure 5. FTIR spectra of the GQDs produced using (a) various NaOH concentrations (b) different reaction times, and (c) different voltages.

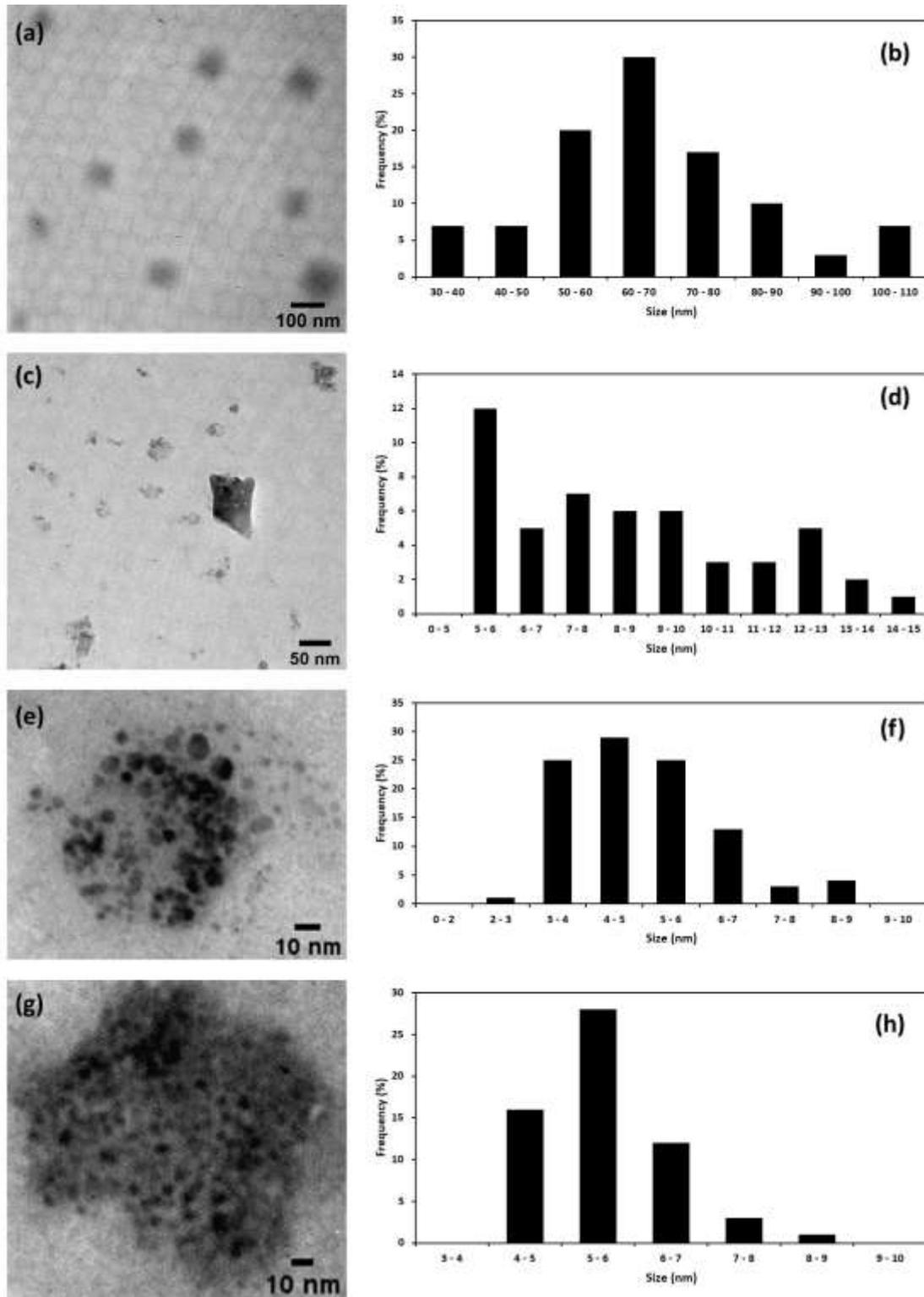


Figure 6. TEM images and size distribution of GQD1 (a – b), GQD2 (c – d), GQD3 (e – f) and GQD4 (g – h), respectively.

Transmission Electron Microscopy (TEM)

Based on the previous analysis, it was found that the optimum GQDs was produced using a voltage of 10 V with 2 hours of reaction time. Therefore, GQD1-GQD4 samples were selected for imaging and morphology analyses using transmission electron

microscopy (TEM). The TEM images and distribution of diameter or size of the GQDs suspensions obtained are shown in Figure 6. Figure 6a shows the TEM image of the GQDs produced from the 1:1.5 ratio of citric acid:NaOH electrolyte (GQD1), which are circular in shape with sizes ranging from ~30 nm to ~110 nm. The size distribution is shown in Figure 6b

which indicates that GQD1 possessed a broad range and large particle sizes. The average size of the GQDs was found to be around 67.5 nm and this imply that the electrolytic ratio of 1:1.5 is not suitable for the production of GQDs. The average size, however, is still below 100 nm, which represents the production of graphene nanoflakes instead of graphene quantum dots. The observed large particle diameter could be due to the agglomeration of the GQDs [22]. Figure 6c shows the TEM image of GQDs obtained from the electrolytic ratio of 1:2 citric acid:NaOH. The particle size was observed to range between 5 nm and 15 nm (Figure 6d). Compared to GQD1, the particles in GQD2 were observed to be irregular in shape but smaller in size. Meanwhile, the TEM image of the GQD3 sample shown in Figure 6e indicates that the size of the GQDs particles produced range from 2 nm to 9 nm, with an average size of ~5nm. Despite the smaller size of GQDs obtained, aggregation of the small dots can still be observed from the TEM image. Based on Figure 6g, the size of the GQD4 obtained ranging from 4 nm to 9 nm and the agglomeration is nevertheless more accentuated. The particle size of the GQDs can be affected by varying the ratio of citric acid:NaOH, as observed by the reduction of particle size from GQD1 to GQD3. The prominent aggregation of GQD4 with similar size range as compared to GQD3, showed that GQD3 could be the optimum ratio (of the electrolyte) for the production of GQDs.

CONCLUSION

In conclusion, GQDs were successfully exfoliated from graphite rods via a facile one-step electrochemical exfoliation method. The colour of the electrolyte changed from a colourless solution to a yellow or brown solution which indicated the exfoliation and production of GQDs. The higher the anion concentration of NaOH used in the electrolyte, the higher the amount of GQDs produced and exfoliated. Based on UV-Vis analysis, significant UV absorption peaks were observed between 240-255 nm which depicts the $\pi \rightarrow \pi^*$ transition of the aromatic sp^2 C-C bonds and shoulder peaks between 359-385 nm corresponding to the $n \rightarrow \pi^*$ transition of the C=O bonds. FTIR analysis indicated that the GQDs showed significant absorption around 1635 cm^{-1} due to the stretching of C-C bond (in the aromatic ring). The morphology and the dots shape of the GQDs can be observed under TEM analysis with size range varying according to the combination ratio of citric acid and NaOH as electrolyte. This study also revealed the viability of the production of GQDs via the exfoliation mechanism without the introduction of any heating treatment of the electrode as previously reported using the same electrolyte combination, thus allowing a greener

approach by avoiding high energy consumption.

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REFERENCES

1. Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., Grigorieva, I. V. and Firsov, A. A. (2004) Electric field effect in atomically thin carbon films. *Science*, **306(5696)**, 666–669.
2. Phiri, J., Gane, P. and Maloney, T. C. (2017) General overview of graphene: Production, properties and application in polymer composites. *Materials Science and Engineering B: Solid-State Materials for Advanced Technology*, **215**, 9–28.
3. Ponomarenko, L. A., Schedin, F., Katsnelson, M. I., Yang, R., Hill, E. W., Novoselov, K. S. and Geim, A. K. (2008) Chaotic dirac billiard in graphene quantum dots. *Science*, **320(5874)**, 356–358.
4. Zhu, S., Song, Y., Zhao, X., Shao, J., Zhang, J. and Yang, B. (2015) The photoluminescence mechanism in carbon dots (graphene quantum dots, carbon nanodots, and polymer dots): current state and future perspective. *Nano Res*, **8(2)**, 355–381.
5. Valappil, M. O., Pillai, V. K. and Alwarappan, S. (2017) Spotlighting graphene quantum dots and beyond: Synthesis, properties and sensing applications. *Applied Materials Today*, **9**, 350–371.
6. Pan, D., Zhang, J., Li, Z. and Wu, M. (2010) Hydrothermal route for cutting graphene sheets into blue-luminescent graphene quantum dots. *Advanced Materials*, **22(6)**, 734–738.
7. Peng, J., Gao, W., Gupta, B. K., Liu, Z., Aburto, R. R., Ge, L., Song, L., Alemany, L. B., Zhan, X., Gao, G., Vithayathil, S. A., Kaiparettu, B. A., Marti, A. A., Hayashi, T., Zhu, J. J. and Ajayan, P. M. (2012) Graphene quantum dots derived from carbon fibers. *Nano Letters*, **12(2)**, 844–849.
8. Shin, Y., Lee, J., Yang, J., Park, J., Lee, K., Kim, S., Park, Y. and Lee, H. (2014) Mass production of graphene quantum dots by one-pot synthesis directly from graphite in high yield. *Small*, **10(5)**, 866–870.

9. Fu, Y., Gao, G. and Zhi, J. (2019) Electrochemical synthesis of multicolor fluorescent N-doped graphene quantum dots as a ferric ion sensor and their application in bioimaging. *J. Mater. Chem. B*, **7(9)**, 1494–1502.
10. Dong, Y., Shao, J., Chen, C., Li, H., Wang, R., Chi, Y., Lin, X. and Chen, G. (2012) Blue luminescent graphene quantum dots and graphene oxide prepared by tuning the carbonization degree of citric acid. *Carbon*, **50(12)**, 4738–4743.
11. Yan, X., Cui, X. and Li, L. (2010) Synthesis of large, stable colloidal graphene quantum dots with tunable size. *Journal of the American Chemical Society*, **132(17)**, 5944–5945.
12. Lu, J., Yeo, P. S. E., Gan, C. K., Wu, P. and Loh, K. P. (2011) Transforming C₆₀ molecules into graphene quantum dots. *Nat. Nanotechnol.*, **6(4)**, 247–252.
13. Tan, X., Li, Y., Li, X., Zhou, S., Fan, L. and Yang, S. (2015) Electrochemical synthesis of small-sized red fluorescent graphene quantum dots as a bioimaging platform. *Chemical Communications*, **51(13)**, 2544–2546.
14. Muthurasu, A., Dhandapani, P. and Ganesh, V. (2016) Facile and simultaneous synthesis of graphene quantum dots and reduced graphene oxide for bio-imaging and supercapacitor applications. *New Journal of Chemistry*, **40(11)**, 9111–9124.
15. Li, Y., Li, S., Wang, Y., Wang, J., Liu, H., Liu, X., Wang, L., Liu, X., Xue, W. and Ma, N. (2017) Electrochemical synthesis of phosphorus-doped graphene quantum dots for free radical scavenging. *Physical Chemistry Chemical Physics*, **19(18)**, 11631–11638.
16. Ahirwar, S., Mallick, S. and Bahadur, D. (2017) Electrochemical method to prepare graphene quantum dots and graphene oxide quantum dots. *ACS Omega*, **2(11)**, 8343–8353.
17. Danial, W. H., Chutia, A., Majid, Z. A., Sahnoun, R. and Aziz, M. (2015) Electrochemical synthesis and characterization of stable colloidal suspension of graphene using two-electrode cell system. *AIP conference proceedings*, **1669**, 020020.
18. Zhu, S., Song, Y., Zhao, X., Shao, J., Zhang, J. and Yang, B. (2015) The photoluminescence mechanism in carbon dots (graphene quantum dots, carbon nanodots, and polymer dots): current state and future perspective. *Nano Res.*, **8(2)**, 355–381.
19. Silekaite, A., Puiso, J., Prosycevas, I. and Tamulevicius (2009) Investigation of silver nanoparticles formation kinetics during reduction of silver nitrate with sodium citrate. *Materials Science*, **15(1)**, 21–27.
20. Kim, J. K., Kim, S. J., Park, M. J., Bae, S., Cho, S., Du, Q. G., Wang, D. H., Park, J. H. and Hong, B. H. (2015) Surface-engineered graphene quantum dots incorporated into polymer layers for high performance organic photovoltaics. *Scientific reports*, **5**, 14276.
21. Kim, K. W., Kim, B. S., Lee, S. W., Chung, D. C. and Kim, B. J. (2017) Effects of synthesis pressure conditions on the preparation of graphene-like carbonaceous materials from organic liquid precursors by a solvothermal method. *Carbon Letters*, **23**, 74–78.
22. Pedrero, M., Campuzano, S. and Pingarrón J. M. (2017) Quantum dots as components of electrochemical sensing platforms for the detection of environmental and food pollutants: A review, *Journal of AOAC Int.*, **100(4)**, 950–961.