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Green synthesis of graphene quantum dots from rice flour

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Abstract. Graphene Quantum Dots (GQDs) were successfully synthesized by a green and eco-friendly synthetic method using abundant and naturally available raw materials from rice flour. This study suggested and compared two aggressive approaches to fabricate GQDs, which are hydrothermal method at 170 °C for 8 h and microwave irradiation method at 900 W with a short reaction time of 30 min. The results showed that the hydrothermal method produced GQDs with better nanoparticle size and properties than the microwave irradiation method. Furthermore, the products were only GQDs, water and carbide precipitate, thus avoiding complicated post-processing steps. The synthesized GQDs were determined for their morphology by Transmission electron microscope (TEM) showing spherical nanoparticles with an average size of ~5-7 nm and ~10-14 nm for hydrothermal and microwave irradiation methods, respectively. Besides, these GQDs were also analyzed for their characterizations, morphologies and compositions by UV-vis, XRD and FTIR. Thanks to their low cytotoxicity, good optical stability, and excellent photo-luminescence property, GQDs have become novel nanostructured materials in many application fields from energy to biomedicine and environment such as sensors, bio-imaging, drug carriers, and solar cells.

Keywords: graphene quantum dots (GQDs), photocatalyst, hydrothermal method, microwave irradiation method, rice flour.

Classification numbers: 1.3.3, 2.5.1, 2.1.1.

1. INTRODUCTION

Recently, many studies have targeted the conversion of 2D graphene into 0D GQDs and investigated the impact of edge effects as well as quantum confinement on the properties of this novel material [1-4]. Graphene, discovered by Novoselov *et al.* in 2004 [5], is a new kind of nanomaterial with excellent mechanical, electrical, thermal, and optical properties [6-9], following 0D fullerenes [10,11] and 1D-carbon nanotubes [12-15]. GQDs are a novel 0D

nanomaterial made from graphene that was first reported by Peng *et al*. and are 0D graphene segments that are small enough to exhibit quantum confinement and size effect. Moreover, GQDs also possess size-dependent strong photoluminescence properties. GQDs have been widely studied and considered as a new kind of quantum dots (QDs) because their intrinsically inert carbon properties lead to the exhibiting of their chemically and physically stable properties. Furthermore, GQDs are environmentally friendly due to its non-toxic and biologically inert properties. GQDs are small graphene fragments, with particle sizes in the range of 3 - 20 nm, and favorable surface grafting that involves π–π conjugations.

Compared with its corresponding 2D structure graphene, GQDs offer several unique advantages such as larger dispersibility, richer active sites (edges, functional groups, dopants, etc.), better testability in terms of physicochemical properties and size equivalent to biomolecules, thus GQDs have a lot of potential for application in new fields. Actually, most of the prepared GQDs also contain oxygen and hydrogen, and often have multiple atomic layers, with sizes being less than 10 nm [16, 17]. The band gap energy of the GQDs can be regulated from 0 to 6 eV by changing the 2D size or surface chemical properties, due to the quantum confinement effect of conjugated π-domains and the edge effect.

Besides that, when compared to the QDs of a traditional semi-conductor, GQDs are a new type of carbon material, which has attracted attention for its stable fluorescence properties [18 - 21], large surface area, low toxicity [22 - 25] and hydrophilic nature (good water solubility) [26, 27], good biocompatibility and excellent optical stability. Among them, the fluorescence characteristic is the most important feature of GQDs. In addition, GQDs have many other unique properties such as absorption, electroluminescence and photoluminescence, as well as their electronic and crystallographic properties [28].

GQDs are a promising alternative and can also be used in other applications, such as photovoltaic, organic display devices, and energy storage systems [29]. When compared to other inorganic QDs materials, GQDs have a great advantage of biocompatibility. They are also widely used in life sciences, for instance, in bioimaging (single-photon and multiphoton), biosensing, and possibly cancer treatments, because of their good photoluminescence quantum yield (QY), low toxicity, and excellent resistance to photodegradation [30]. GQDs are also used in environmental monitoring as well as in thermal interface materials [31].

Nowadays, GQDs have been rapidly synthesized by hydrothermal and microwave irradiation methods from rice flour which was utilized as a green precursor in the synthesis. These methods have many advantages as follows: (1) green and low-cost raw materials; (2) no use of a strong acid or base; (3) no metal impurity and no toxic gases produced; (4) simple operation and short reaction time; and (5) no need for complicated post-processing steps [32]. Specifically, hydrothermal synthesis is one of the most commonly used methods for the synthesis of nanomaterials. Using hydrothermal method can produce unstable nanomaterials at high temperatures [33]. Hydrothermal synthesis has received great attention because of its high controllability over the composition, size and shape of the resulting nanomaterials. Furthermore, the combination with water as a reaction medium, instead of exotic solvents with high boiling points, makes hydrothermal method more environmentally friendly than other methods [34]. The synthesis of GQDs by hydrothermal method has the advantages of a simpler, safer and more feasible process and the possibility of large-scale production [35]. Besides, GQDs produced by this technique have a large number of oxidizing groups (e.g. carboxyl, hydroxyl and epoxy groups) at their edges and base planes, making them dispersable in the aquatic environment [36]. A minor drawback of this procedure is that it is difficult to monitor the interactions between the reactants as the reaction takes place. On the other hand, microwave radiation is also of interest in

the synthesis of nanoparticles in general and GQDs in particular because it combines the advantages of rapid reaction rates and homogeneous heating of precursor materials [37]. Thanks to the penetrating property of radiation, this method can homogeneously heat the reaction solution leading to the formation of nanoparticles with a small size and uniform distribution [38]. Compared with other conventional methods, microwave irradiation synthesis has the advantage of a short reaction time, since the synergistic forces generated by both electrical and magnetic components of the microwave produce friction and collisions of molecules [39].

To the best of our knowledge, there have been no published reports concerning the comparison of the ability to synthesize GQDs and the properties of GQDs produced by these two methods. Herein, GQDs were successfully synthesized by both hydrothermal and microwave irradiation methods. Furthermore, the properties of this nanomaterial were also analyzed.

2. MATERIALS AND METHODS

2.1. Materials

Ascorbic acid ($C_6H_8O_6$, 99.7 %) was bought from Sigma-Aldrich (USA) and Rice flour of Tai Ky Food - Flour Jsc. (Viet Nam) was purchased at Can Tho city. All solutions were prepared with deionized water (DI H_2O) from a MilliQ system.

2.2. Synthesis of GQDs

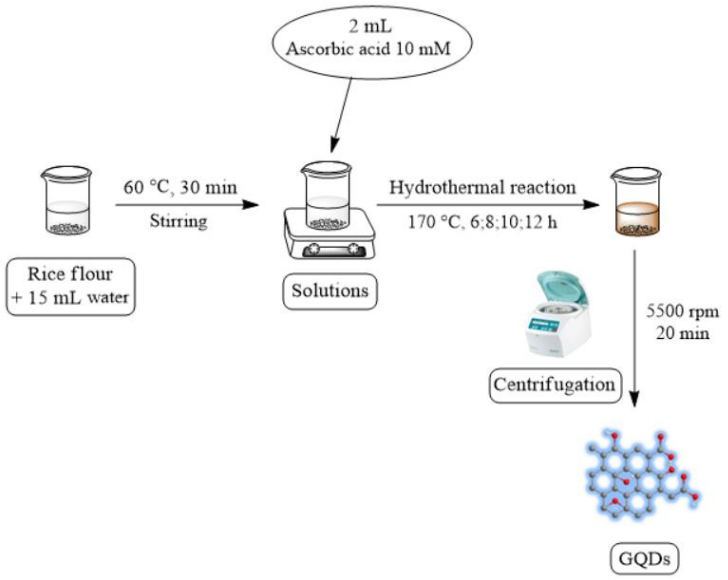
Natural polymer starch was used as a new precursor in GQDs synthesis. No strong acids or any other oxidizing agents and metal impurities were used as reactants. Additionally, the products are only GQDs, water and carbide precipitate. Thus, complicated post-processing was not required since the precipitate could be easily separated from the GQDs solution.

Preparation of GQDs by hydrothermal method

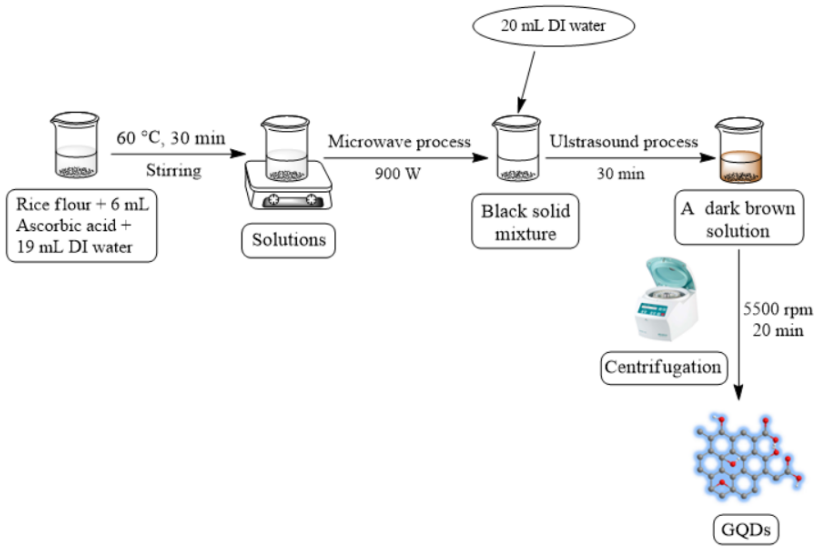
First, 0.1 g of rice flour was completely dispersed in 15 mL of deionized water (DI H_2O) and stirred at 60 °C for 30 min. Next, 2 mL of ascorbic acid (10 mM) was added and continued stirring for 5 min. After dissolved, the solution was immediately poured into a Teflon-lined stainless autoclave, which was heated in an oven at 170 °C for various reaction times. Then, the autoclave was taken out to be cooled freely. The final brown product was transferred into centrifugal tubes and centrifuged at 5500 rpm for 20 min to separate out the precipitate. The pale yellow liquid obtained was the solution of GQDs, which was stored at 8 °C for use in the next step.

Preparation of GQDs by microwave irradiation method

First, a mixture of rice flour with 6 mL of ascorbic acid (0.5682 M) and 19 mL of deionized water (DI H_2O) in a 100 mL beaker was stirred at 60 °C for 30 min to obtain a homogeneous solution. Then, the microwave process was conducted at 900 W for various reaction times. A dark brown solid obtained was allowed to cool naturally. The solid mixture was mixed with 20 mL of deionized water (DI H_2O), then sonicated for 30 min to obtain a dark brown solution, which was centrifuged at 5500 rpm for 20 min to remove insoluble solids. After centrifugation, GQDs solution was obtained. Finally, the synthesized GQDs were stored at 8 °C for characterization.



*Scheme 1.*The process of synthesizing GQDs by hydrothermal method.



*Scheme 2.*The process of synthesizing GQDs from rice flour and ascorbic acid by microwave irradiation method.

2.3. Characterizations of GQDs

The GQDs synthesis was observed by recording the absorbance spectra between 200 and 900 nm on a UV-vis spectrophotometer (Thermo Scientific Evolution 60S UV-Vis spectrophotometer, USA). X-ray diffraction (XRD) was performed on a D8-Advance machine (Bruker, Germany) in the 2θ range of 10°-90°. The Fourier transform infrared (FT-IR) spectra were obtained by Perkin Elmer Frontier MIR/NIR (Perkin Elmer, USA) conducted in KBr pellet

at room temperature in the range of 4000 - 400 cm^{-1}. Transmission electron microscopy (TEM) characterization was performed on a JEM1010 device (JEOL Company, Japan).

2.4. Statistical analysis

All experiments and analyses were conducted in triplicate to confirm the results. The results were expressed as average data from three measurements.

3. RESULTS AND DISCUSSION

3.1. UV-vis Spectral Analysis

With the hydrothermal method, the maximum absorption intensity of the GQDs samples has an absorption wavelength in the range from 305 nm to 315 nm as shown in Figure 1A.

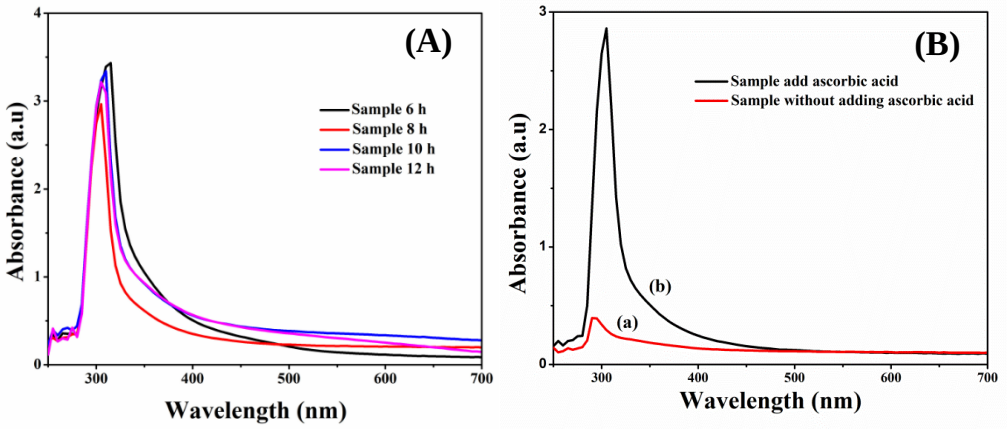


*Figure 1.*UV-vis spectra of GQDs by hydrothermal method: (A) at different reaction times: 6 h, 8 h, 10 h, 12 h; (B) without (a) and with (b) ascorbic acid reducing agent.

It is clear that the heating time has an effect on the formation of GQDs. When the time prolongs, the excitation energy for the system increases, making the carbonization process take place faster and consequently the amount/concentration of GQDs formed in the solution increases as well. Meanwhile, the prolonged heating time also causes large effects on the structure of GQDs material. Because the carbonization and oxidation processes occur greatly, the characteristic optical properties of GQDs decrease, making the formation of GQDs nanoparticles in the solution decrease gradually. With an 8 h reaction time, a characteristic peak of synthesized GQDs has very clear sharpness and narrower width than other peaks. This shows that the nanoparticles were uniformly formed and had better optical properties than the remaining samples. The effect of ascorbic acid (AA) reductant on the reaction was also investigated. Figure 1B indicates that the maximum absorption intensity of the sample added with AA has the highest wavelength at 305 nm (Figure 1B(a)) and the sample without adding AA at 290 nm (Figure 1B(b)). In addition, the maximum absorption peak of GQDs synthesized from rice flour and AA is clear and much higher than that of the sample without added acid. This shows that the amount of reductant (reducing agent) in the reaction solution affects the formation of the obtained GQDs nanoparticles. Indeed, AA is the source of H^+ for hydrolyzing starch into glucose to synthesize GQDs under the support of the hydrothermal process.

Conclusively, the presence of AA reductant helps the GQDs formation reaction happen completely and successfully.

On the other hand, the influence of reactive factors in the synthesis of GQDs by microwave irradiation method was also evaluated. The UV-Vis results show that the maximum absorption intensity of the GQDs samples has wavelengths in the range from 300 nm to 315 nm as shown in Figure 2A**.** The maximum absorption intensity of the GQDs samples on the UV-vis spectrum reaches the highest wavelength at 315 nm corresponding to the GQDs samples using 0.1 g of rice flour. It can be predicted that the amount of reactant used in the pre-reaction solution affects the absorption intensity of the post-synthesis sample. Rice flour is the main raw material used for the synthesis of GQDs, so increasing the amount of initial starch leads to increasing the amount/concentration of GQDs formed. But when the rice flour is too much, the glucose concentration will be higher and many adjacent glucose molecules bind together, making the GQDs large in size and reducing the absorption intensity. Therefore, 0.1 g of rice flour was selected as the optimal sample for the synthesis of GQDs. Heating time also affects the reaction (Figure 2B). With different reaction times, the GQDs samples have an absorption wavelength in the range of 295 nm to 315 nm. Specifically, for 15 min of reaction (Figure 2B(b)), the GQDs obtained the highest maximum absorption intensity compared to the remaining samples. This can be explained when the microwave treatment time is prolonged the excitation energy for the system also increases, making the carbonization process take place faster, leading to an increase in the amount/concentration of the formed GQDs in the solution. Meanwhile, when the microwave treatment time is too long, it will greatly affect the structure of GQDs because the carbonization and oxidation processes occur too much, leading to a decrease in the characteristic optical properties of GQDs.

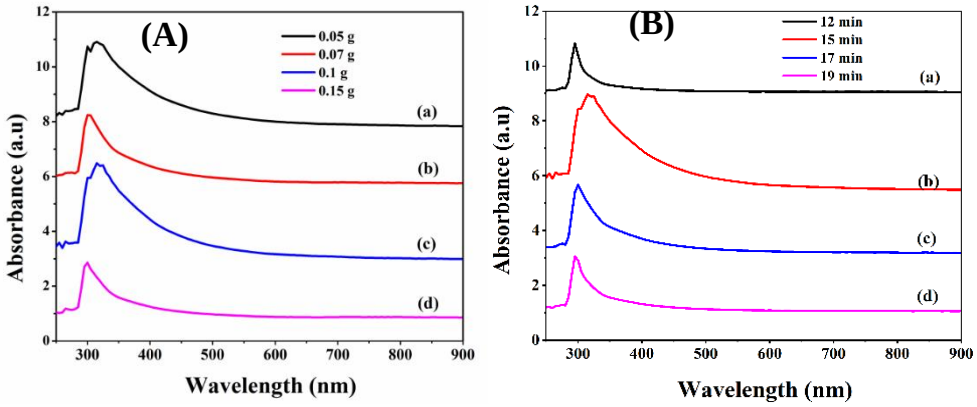


Figure 2. UV-vis spectra of GQDs by microwave irradiation method: (A) with different amounts of rice flour respective to: (a) 0.05 g; (b) 0.07 g; (c) 0.1 g and (d) 0.15 g, and (B) at various reaction times: (a) 12 min; (b) 15 min; (c) 17 min and (d) 19 min.

In addition, Figure 3 shows that the maximum absorption peak of the optimal sample GQDs synthesized by the hydrothermal method is at 305 nm while that synthesized by the microwave irradiation method is 315 nm. GQDs synthesized by microwave irradiation method (Figure 3(a)) obtained a higher maximum absorption intensity compared to the remaining method. However, its absorption intensity shows no significant change in the range of 305 - 315 nm, and the maximum absorption peak is not as clear and smooth as the peak of GQDs synthesized by the hydrothermal method (Figure 3(b)). This can be explained by the shorter microwave treatment

time: the treatment occurs quickly in only 15 min at 900 W, meanwhile, with the hydrothermal method the solution is heated for 8 h at 170 °C. Therefore, it can be predicted that the hydrothermal method can supply enough excitation energy for the system, making the oxidation and carbonization processes take place completely, leading to better properties of the formed GQDs than the microwave irradiation method.

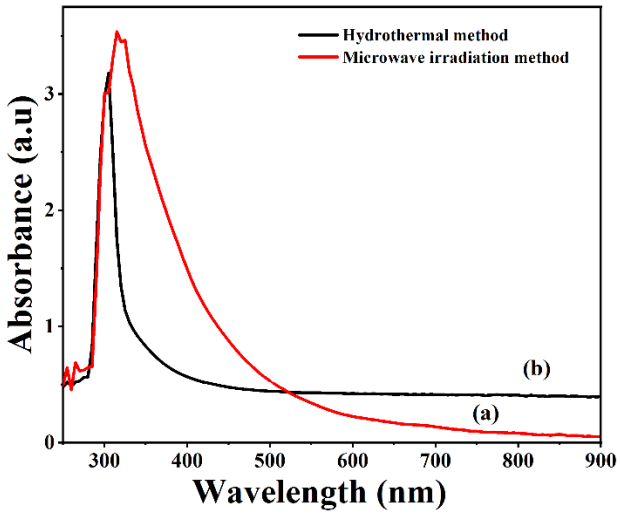


Figure 3. UV-vis spectra of GQDs by: (a) Microwave irradiation method, (b) Hydrothermal method.

3.2. XRD analysis

Figure 4 shows the typical X-ray diffraction patterns for as-synthesized GQDs.

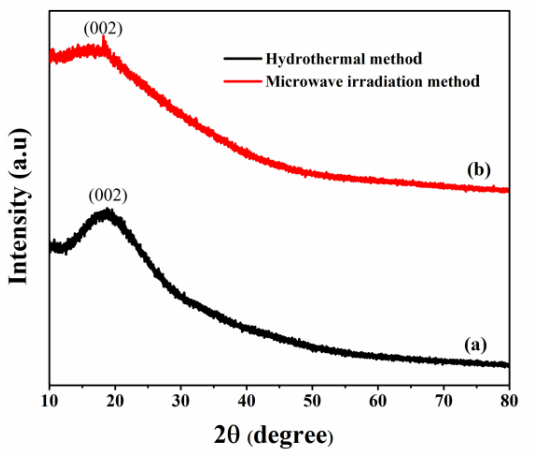


Figure 4. XRD patterns of GQDs by: (a) Hydrothermal method, and (b) Microwave irradiation method.

The XRD patterns of GQDs show a broad peak at around 20° corresponding to the hexagonal graphite plane of (002). The position and intensity of these diffraction peaks of GQDs are often highly dependent on the presence of hydroxyl, epoxy, carbonyl and carboxylic groups,

which increase the distance between the carbon plates [40]. Moreover, there are similarities in the XRD results of GQDs made up of hydrothermal and microwave irradiation methods, indicating that both methods studied can be applied to successfully synthesize GQDs.

3.3. FTIR analysis

The existence of chemical functional groups of GQDs is evidenced by FTIR infrared spectra (Figure 5). From the obtained results, it can be confirmed that the FTIR spectral characteristics of the synthesized GQDs nanomaterial are consistent with those of the GQDs published in previous researches [32, 40].

As shown in the FTIR spectra of the GQDs synthesized by hydrothermal method (Figure 5(b)), the peak appeared at 3313 cm^{-1} characterizes for O-H functional groups [41] which are important functional groups that facilitate the hydrophilicity and stability of GQDs. The peak at 2888 cm^{-1} is characteristic for C–H and that at 2298 cm^{-1} is characteristic for the oscillation of –O–C=O. Peaks at 1652 cm^{-1} and 1420 cm^{-1} are characteristic for –C=C– and C–C groups, respectively. Besides, peaks at 1076 cm^{-1} and 1033 cm^{-1} are typical peaks for oscillationof C–O groups. On the other hand, Figure 5(a) shows the FTIR spectrum of the GQDs obtained by microwave irradiation method, the peak at 3288 cm^{-1} is typical for O-H functional groups [41] which are important functional groups that facilitate the hydrophilicity and stability of GQDs. The peak at 2887 cm^{-1} is the characteristic peak for C–H and peaks at 2301 cm^{-1} and 1760 cm^{-1} are characteristic for –O–C=O and C=O groups, respectively. Peaks at 1691 cm^{-1} and 1340 cm^{-1} are characteristic peaks for the bonds corresponding to C=O and C–H groups. Besides, the peaks at 1145 cm^{-1} and 1043 $cm^{-1}$are characteristic peaks for the stretching vibrations of the bonds corresponding to C–O groups.

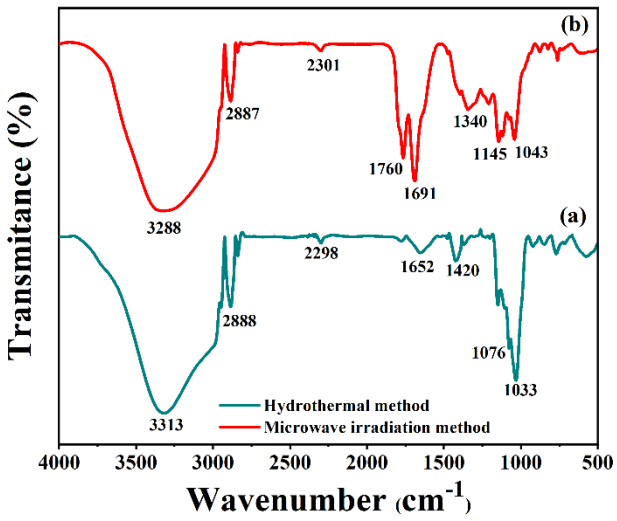


Figure 5. FTIR infrared spectrum of GQDs by: (a) Microwave irradiation method, and (b) Hydrothermal method.

FTIR spectra also confirm the presence of oxygen-containing functional groups, epoxy and carboxyl groups in the GQDs sample. In conclusion, FTIR spectra showed that GQDs were completely synthesized by both hydrothermal and microwave irradiation methods.

3.4. Morphological study

The structure and morphology of GQDs were further confirmed by transmission electron microscopy (TEM) as shown in Figure 6. TEM analysis confirmed the presence of spherical morphology of the nanoparticles corresponding to GQDs synthesized from both methods. Besides, the particle size distribution histogram (Figure 6A(b)) shows that GQDs synthesized by hydrothermal method have an average particle size of ~ 5 - 7 nm. Meanwhile, the average particle size ~10 - 14 nm corresponds to the GQDs samples synthesized by microwave irradiation method (Figure 6B(b)). This shows that the synthesized GQDs have a shape and size consistent with typical GQDs, which are in good agreement with the previous studies.

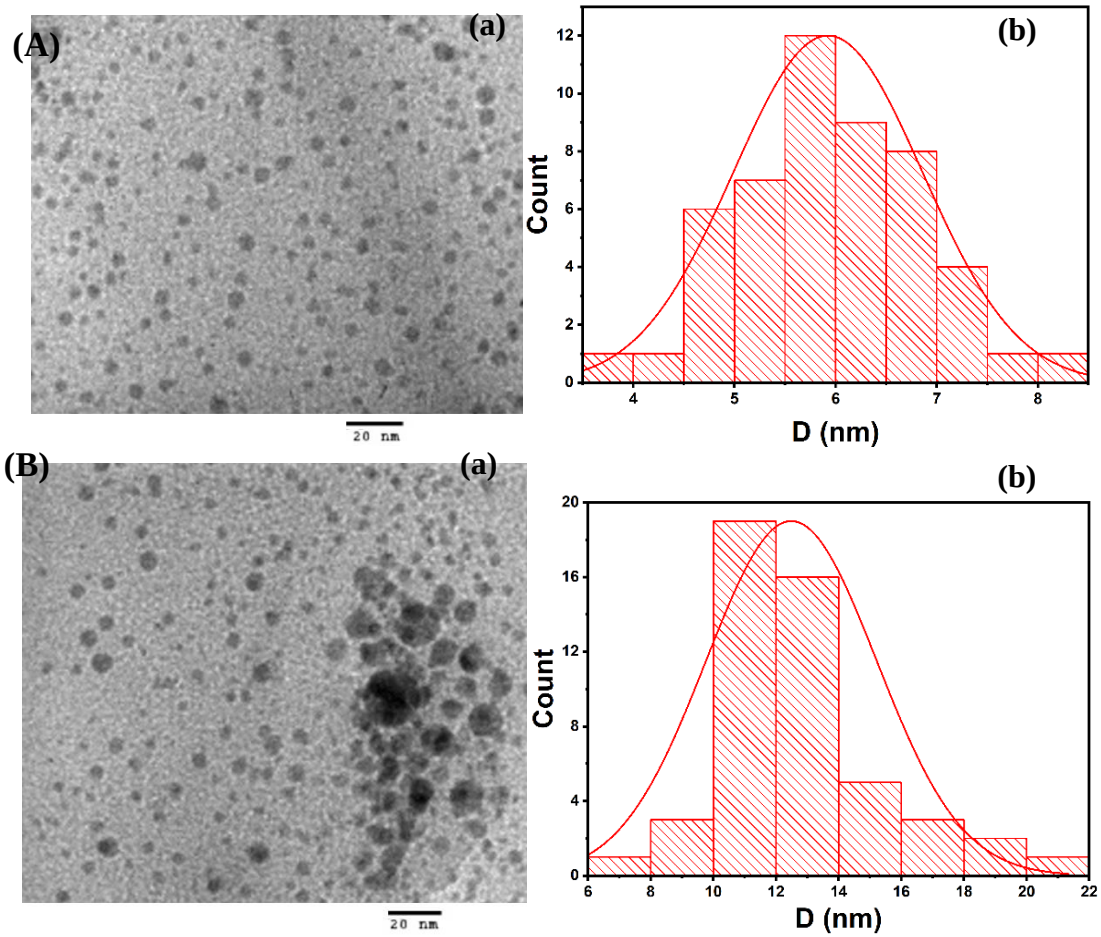


Figure 6.(A) TEM image (a) and particle size distribution(b) of GQDs synthesized by hydrothermal method; (B) TEM image (a) and particle size distribution(b)of GQDs synthesized by microwave irradiation method.

Especially, the results also indicate that the sample synthesized by the hydrothermal method would exhibit particles with a smaller size (~5-7 nm) and more uniform than the sample synthesized by the microwave irradiation method (~10-14 nm). Therefore, the hydrothermal method is suggested as the better way to generate GQDs by this study.

4. CONCLUSIONS

In this study, with an environmentally friendly approach, Graphene Quantum Dots (GQDs) were successfully synthesized by green chemistry method (simple, easy to implement, short reaction time) under hydrothermal reaction and microwave process. Moreover, rice flour was used as a new friendly precursor to fabricate GQDs. From the analysis results of the obtained optimal GQDs, the morphologies of the particles observed by TEM indicated that the size of the GQDs nanoparticles synthesized by hydrothermal method (~5-7 nm) is smaller and more uniform than that of the particles synthesized by microwave irradiation method (~10-14 nm). In other words, GQDs nanoparticles can be synthesized more successfully by hydrothermal method than by microwave irradiation method. This is one of the most eco-friendly methods to synthesize GQDs with high emission and facilitates the application of GQDs in cell imaging, medical, optical and energy-related fields, etc.

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CRediT authorship contribution statement.Tran Thi Bich Quyen: Methodology, Investigation, Funding acquisition, Supervision. Huynh Thi Thuy Phuong: Formal analysis, Data collection, Data analysis. Ngo Nguyen Tra My: Data analysis, Writing and Editing manuscript. Doan Van Hong Thien: Visualization, Supervision. Luong Huynh Vu Thanh and Tran Nguyen Phuong Lan: Review and Editing.

Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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