Chapter 70

GQD purification study obtained by bottom-up route aiming at the production of photocatalysts

https://doi.org/10.56238/methofocusinterv1-070

Luiz Gustavo Sakaguti
State University of Maringá - Department of Chemical Engineering, Maringá, Brazil

Leonardo Zavilenski Fogaça
State University of Maringá - Department of Chemical Engineering, Maringá, Brazil

Camila Fabiano de Freitas
Federal University of Santa Catarina - Department of Chemistry, Florianópolis, Brazil

Wilker Caetano
State University of Maringá - Department of Chemistry, Maringá, Brazil

Vagner Roberto Batistela
State University of Maringá - Department of Pharmacology and Therapeutics, Maringá, Brazil

Mara Heloisa Neves Olsen Scaliante
State University of Maringá - Department of Chemical Engineering, Maringá, Brazil

ABSTRACT
Recent studies have shown that heterostructures composed of metal semiconductors (SC) and graphene quantum dots (*QDs*) have a photocatalytic performance considerably higher than that of intrinsic metallic semiconductors, this is *because the GQDs* reduce the electronic recombination on the surface of the CS, being still associated with the displacement of the absorption band to larger wavelengths. In the present work, graphene quantum dots were synthesized through commercial lignin (LcGQD), using nitric acid for depolymerization followed by a hydrothermal process. Analyses of the material demonstrated an average particulate size of 10.9 nm, UV-Vis absorption similar to that of other structures described in the literature, but without the presence of nitrogen peaks in the carbon structure, besides a remarkable specificity in fluorescence. The LcGQD then has great potential for use in photocatalysis, sensors, and optoelectronics.

Keywords: Graphene quantum dots, nanomaterials, lignin.

1 INTRODUCTION

Graphene has gained high popularity in the scientific environment due to the electrical, thermal, and mechanical properties that give the material an extremely promising future in the areas of electronics, energy, and the environment(NEMATI et al., 2022). In particular, graphene quantum dot (*QD*), a nanomaterial of zero dimension (0 D) with even more specific characteristics because it is chemically inert, has extremely small size, is highly soluble and photoluminescent (KANSARA et al., 2022). These characteristics allow the use of the material in the fields of optoelectronics, medical imaging, solar cells, and photocatalysis(TIAN et al., 2018).

The synthesis of graphene quantum dots, despite having a certain simplicity, usually require a large amount of time and a large number of steps, in which the use of strong acids, organic solvents, high pressures, and temperatures are often used(RUSSO et al., 2016). Among the types of synthesis of *The DQS*, there are two main categories, these being *top-down* and *bottom-up*. The *top-down method* obtains the nanoparticles by reducing the material into smaller sizes while *the bottom-up* consists of the grouping of previously disorganized molecules and atoms into organized nanostructures(ABID et al., 2022; BISWAS et al., 2012). *Top-down synthesis routes* despite presenting a greater simplicity of obtaining nanoparticles, present a high cost, severe conditions, and long reaction time, in addition, there is a great difficulty in controlling size, morphology, and functional groups present, while the *bottom-up method* usually exhibits a more uniform distribution of particulate size and still allows the use of a wider range of precursors, such as biomass, however, requires more complex methods with lower conversions(GAO et al., 2020; SHARMA; DAS, 2019; YANG et al., 2023).

The hydrothermal method involves applying high temperatures and vapor pressures so that the process of breaking down and particle size decreases occurs. The hydrothermal method is also the most widely used for bottom-up synthesis, and researchers consider it cheap, ecological, and low-cost for GQD synthesis (SHARMA; DAS, 2019). In general, it is the simplest synthesis route for the manufacture of GQD, which may involve the use of alkaline agents (NaOH or ammonia) to aid the breakdown of the precursors of GO (PAN et al., 2010). Tian et al., 2016 advocate the use of strong oxidizing agents such as HNO_3, H_2SO_4, or H_2O_2 during hydrothermal synthesis (TIAN et al., 2016). There is a certain interest in the use of these agents because, in addition to assisting in the exfoliation and breaking of carbon particles, they can also affect the final properties of The DQD through the presence of heteroatoms and functional groups on the surface (XIE; LAI; HUQ, 2017).

The choice of non-renewable precursors such as graphene oxide, carbon fiber, carbon nanotubes, and graphene itself for *the synthesis of GQDs* is usually a limiting fact for the synthesis of nanomaterial, however, the use of biomass for the synthesis of graphene quantum dots has been gaining prominence for being cheap, renewable, carbon-rich and still brings with it an eco-friendly synthesis(ABBAS et al., 2021; WANG et al., 2022). Among the possible precursors of graphene quantum dots from biomass, lignin, according to Gellerstedt et al. (2008), is the second most abundant polymer in nature, presents a high degree of carbon with aromatic structures, making it a great option for the production of *GQDs*(ZHU et al., 2022). Through the surprising results achieved in recent years, the progress made in the area of the development of more sustainable materials based on DQD has been deeply accelerated(ZENG et al., 2018).

Concerning photocatalysis, ZnO and TiO_2 are widely used due to their high oxidation efficiency, chemical stability, non-toxicity, wide application in organic pollutants, and high durability in photocatalysis reactions(SODEIFIAN; BEHNOOD, 2020). However, such photocatalysts have characteristics such as a *high band gap energy*, thus limiting their use in photocatalytic reactions only with UV light, and there is still high electronic recombination, thus reducing their catalytic activity(REHMAN et al., 2009). Thus, to reduce electronic recombination and improve the absorption of visible light in metallic semiconductors (SC), researchers have demonstrated a significant improvement in obtaining heterostructures of these with graphene quantum dots, demonstrating a promising future for nanomaterial in photocatalysis(CUI et al., 2022; LIU et al., 2021; WANG et al., 2021a).

The main objective of this work was the production of QD from commercial alkaline lignin (LcGQD) through the hydrothermal method and doping of the carbon structure by the use of oxidizing agent (HNO_3). After synthesis, the material was submitted to dialysis for evaluation of this process in the homogenization of particulate size, and other characterizations such as DLS, UV-Vis, and Fluorescence.

2 METHODOLOGY

The reagents used in this work were alkaline lignin (4% sulfur, pH 10.5) with an average molecular mass of 10,000 g $^{mol-1}$ Sigma-Aldrich, nitric acid (65%) (Synth), and sodium hydroxide (Fmaia gold). None of the reagents mentioned suffered from additional purification processes, being used only in their commercial form.

Synthesis of Lc*GQD*

For the synthesis *of The GQDs*, zhu's adapted hydrothermal method (2022)was used for this, 3 g of alkaline lignin was dispersed in a solution with 9% HNO_3 *so* that there was lignin depolymerization and was maintained in reflux at 80 ºC for 8 h. Then the solution was filtered to vacuum and the acidified lignin retained by the filter was added to a NaOH solution of 0.2 mol $^{L-1}$ and later added to ultrasound for 3 h. Soon after, the solution was added to the autoclave and arranged in a greenhouse at 160 ºC for 8 h.

Purification of *GQDs*

To purify the *GQDs obtained*, the solution removed from the autoclave after the hydrothermal process was filtered through a membrane with pores of 0.22 µm. Then, the filtered solution was transferred to dialysis membranes of 14 kDa and 3.5 kDa for 7 days for filtration of the filtrate.

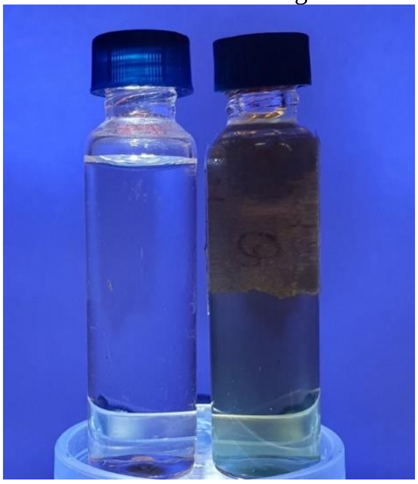
Characterization of *QDs*

For the analysis of the absorbance of the dialyzed samples, a Shimadzu UV-1800 spectrophotometer was used with a scanning range between 200 nm and 800 nm. Regarding particulate size, Dls NanoPlus 3 (liquid sample, at 25 ºC, in triplicate) was used. For fluorescence, Cary Fluorimeter was used with a scan range between 300 and 800 nm with excitation at 350 nm.

3 RESULTS AND DISCUSSION

Aiming to initially test the obtaining of particulates generated in hydrothermal synthesis, UV radiation was designed to perform a preliminary luminescence test. This was preceded by dialysis to verify the presence and stability *of QDs* with UV LED of 365 nm present in Figure 1 points to a clear distinction of luminescence between deionized water (the left) and the Lc-GQD (right). Figure 1 shows that the apparent brown color of the material under visible radiation becomes green when irradiated with UV LED. This test indicates the presence of nanoparticles in suspension, which once excited with UV radiation, emit luminescence at different wavelengths. This assay is effective in determining whether the applied synthesis method was able to produce carbon nanoparticles.

Figure 1. Luminescence of *GQD solution* derived from commercial lignin irradiated with UV LED 365 nm before dialysis.



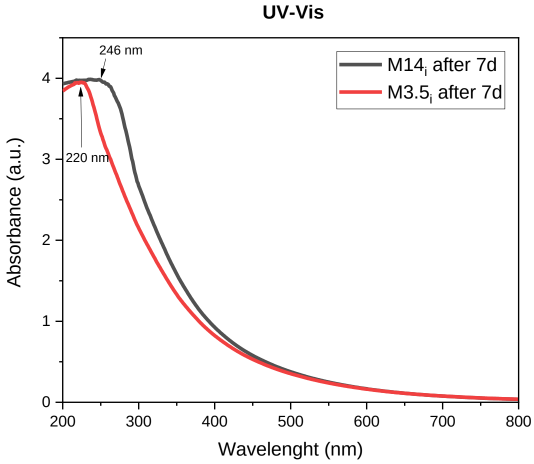
The results obtained through DLS shown in table 1 indicate the particle size distribution (D-90%), the notations used refer to $M14_{and}$ - Particles external to the membrane of 14 kDa, $M14_{i}$ - Particles internal to the membrane of 14 kDa, $M3.5_{and}$ - Particles external to the membrane of 3.5 kDa and $M3.5_{i}$ - Particles internal to the membrane of 3.5 kDa. From the data presented, it is observed that the smallest sizes of the materials obtained are internal to the membranes. Tal facto is justified, according to WANG et al. (2021b) due to possible agglomerations of the nanomaterial in more stable molecules occurring in the external environment to the membrane. Since the particulates filtered by the membranes are very small, it is believed that they are not chemically stable, tending to cluster into larger carbon structures to compensate for this chemical imbalance. Thus, $m14_{i}$ and M3.5i materials have a higher potential for applications in the improvement of photocatalysts, since, according to SILVA et al. (2010), quantum dots have strong quantum confinement, being directly affected by particle size. Further studies should be carried out to interpret the fact that the internal particle membranes acquire the stability necessary to maintain their particle size.

Table 1. Particle size distribution results (D-90%) in lc-GQD nm, after 7d dialysis.

Repetition	$M14_{and}$	M14	$M3.5_{and}$	$M3.5_{I}$
1	59.3	10.9	724,3	64.3
2	157.9	10.9	92,6	13.5
3	22.3	10.9	112.9	13.2
Average	79.8	10.9	309.9	30.3

The absorbance results contained in Figure 2 show a greater displacement of absorption to wavelengths greater than $M14_i$, with peaks at 220 nm for M3. 5i and at 246 nm for $M14_i$, both peaks are related to π-π* transitions related to the sp^2 bonds of the aromatic rings of the particle.

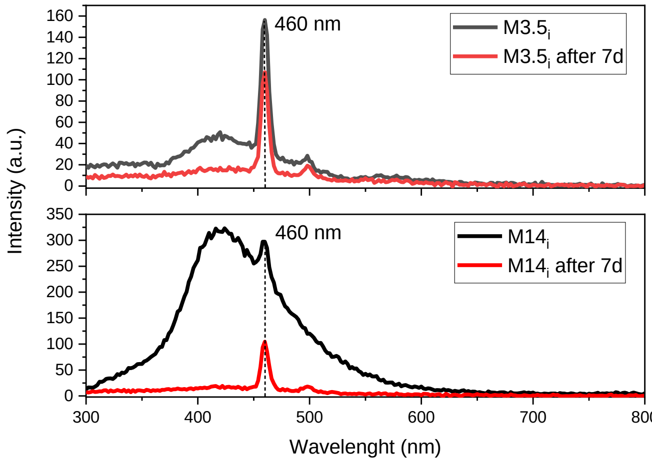
Figure 2. UV-Vis spectra for internal samples to 3.5 kDa and 14 kDa membranes.



In addition, no expected shoulders were observed at longer wavelengths referring to less energetic n-π* transitions caused by the presence of groups containing oxygen and nitrogen from the use of lignin as a precursor and nitric acid in depolymerization, then indicating a low amount of these groups.

The fluorescence results present in Figure 3 indicate the efficiency of dialysis in the purification of the nanoparticle mainly for the 14 kDa membrane due to the high narrowing of the peak regions. Moreover, a remarkable fluorescence specificity can be observed occurring at 460 nm. This narrow range in the emission of the material has extreme significance, as it can guarantee this material various technological applications, mainly for areas of sensors and photocatalysis reactions involving visible light. Thus, the LcGQD obtained in this work after purification with 14kDa membrane can be a promising material for application in heterostructures with metallic semiconductors.

Figure 3. Fluorescence spectrum excited at 350 nm anterior and posterior to dialysis for materials internal to membranes.



4 CONCLUSION

The study in question demonstrated the feasibility of using lignin as a precursor of GQD with good quality, evidencing the great potential of the use of biomass for the production of these nanomaterials. Through a *bottom-up synthesis route with the hydrothermal* process that, despite allowing a reagglomeration of particulates, still produces a material with a good size range, with an average of up to 10.9 nm, being considered eco-friendly. Cawell studies the insertion of functional grouping to stabilize the molecule, thus ensuring a smaller regrouping of the material.

It also verified the importance and efficiency of dialysis as a stage of particulate purification, due to a large narrowing in the fluorescence range of the material. Finally, it is emphasized the obtaining of carbon with a highly specific emission range at 460 nm, having applications provided for in the photocatalyst and other technological areas.

REFERENCES

ABBAS, A. et al. Role of precursor microstructure in the development of graphene quantum dots from biomass. **Journal of Environmental Chemical Engineering**, v. 9, n. 5, p. 106154, 1 out. 2021.

ABID, N. et al. Synthesis of nanomaterials using various top-down and bottom-up approaches, influencing factors, advantages, and disadvantages: A review. **Advances in Colloid and Interface Science**, v. 300, p. 102597, 1 Feb. 2022.

BISWAS, A. et al. Advances in top–down and bottom–up surface nanofabrication: Techniques, applications & future prospects. **Advances in Colloid and Interface Science**, v. 170, n. 1–2, p. 2–27, 15 jan. 2012.

CUI, Y. et al. Graphene quantum dots/carbon nitride heterojunction with enhanced visible-light driven photocatalysis of nitric oxide: An experimental and DFT study. **Carbon**, v. 191, p. 502–514, 1 maio 2022.

GAO, T. et al. Bridge between Temperature and Light: Bottom-Up Synthetic Route to Structure-Defined Graphene Quantum Dots as a Temperature Probe in Vitro and in Cells. **ACS Applied Materials and Interfaces**, v. 12, n. 19, p. 22002–22011, 13 maio 2020.

GELLERSTEDT, G. L. F.; HENRIKSSON, E. G. Lignins: Major Sources, Structure and Properties. **Monomers, Polymers and Composites from Renewable Resources**, p. 201–224, 1 jan. 2008.

KANSARA, V. et al. Graphene quantum dots: Synthesis, optical properties and navigational applications against cancer. **Materials Today Communications**, v. 31, p. 103359, 1 jun. 2022.

LIU, W. et al. Lignin-derived graphene quantum dots from phosphous acid-assisted hydrothermal pretreatment and their application in photocatalysis. **Industrial Crops and Products**, v. 171, p. 113963, 1 nov. 2021.

NEMATI, F. et al. Cerium functionalized graphene nano-structures and their applications; A review. **Environmental Research**, v. 208, p. 112685, 15 maio 2022.

PAN, D.; ZHANG, J.; LI, Z.; WU, M. Hydrothermal Route for Cutting Graphene Sheets into Blue-Luminescent Graphene Quantum Dots. **Advanced Materials**, vol. 22, no. 6, p. 734–738, 9 Feb. 2010. DOI 10.1002/adma.200902825. Available at: https://onlinelibrary.wiley.com/doi/10.1002/adma.200902825.

REHMAN, S. et al. Strategies of making TiO2 and ZnO visible light active. **Journal of Hazardous Materials**, v. 170, n. 2–3, p. 560–569, 30 out. 2009.

RUSSO, P. et al. Single-step synthesis of graphene quantum dots by femtosecond laser ablation of graphene oxide dispersions. **Nanoscale**, v. 8, n. 16, p. 8863–8877, 21 abr. 2016.

SHARMA, A.; DAS, J. Small molecules derived carbon dots: synthesis and applications in sensing, catalysis, imaging, and biomedicine. **Journal of Nanobiotechnology 2019 17:1**, v. 17, n. 1, p. 1–24, 26 ago. 2019.

SILVA, F. O. et al. O estado da arte da síntese de semicondutores nanocristalinos coloidais. **Química Nova**, v. 33, n. 9, p. 1933–1939, 2010.

SODEIFIAN, G.; BEHNOOD, R. Hydrothermal Synthesis of N-Doped GQD/CuO and N-Doped GQD/ZnO Nanophotocatalysts for MB Dye Removal Under Visible Light Irradiation: Evaluation of a New Procedure to Produce N-Doped GQD/ZnO. **Journal of Inorganic and Organometallic Polymers and Materials**, v. 30, n. 4, p. 1266–1280, 1 abr. 2020.

TIAN, P. et al. Graphene quantum dots from chemistry to applications. **Materials Today Chemistry**, v. 10, p. 221–258, 1 dez. 2018.

TIAN, R.; ZHONG, S.; WU, J.; JIANG, W.; WANG, T. Facile hydrothermal method to prepare graphene quantum dots from graphene oxide with different photoluminescences. **RSC Advances**, vol. 6, no. 46, p. 40422–40426, 2016. https://doi.org/10.1039/c6ra00780e.

WANG, G. et al. Construction of heterojuncted photocatalyst with TiO2 quantum dots and graphene oxide nanosheets for highly efficient photocatalysis. **Scripta Materialia**, v. 199, p. 113862, 1 jul. 2021a.

WANG, R. et al. Concentration-dependent emissive lignin-derived graphene quantum dots for bioimaging and anti-counterfeiting. **Diamond and Related Materials**, v. 117, p. 108482, 1 ago. 2021b.

WANG, Y. et al. Synthesis of corn straw-based graphene quantum dots (GQDs) and their application in PO43- detection. **Journal of Environmental Chemical Engineering**, v. 10, n. 2, p. 107150, 1 abr. 2022.

XIE, J. De; LAI, G. W.; HUQ, M. M. Hydrothermal route to graphene quantum dots: Effects of precursor and temperature. **Diamond and Related Materials**, vol. 79, no. July, p. 112–118, 2017. https://doi.org/10.1016/j.diamond.2017.08.014.

YANG, S. et al. Fabrication of Carbon-Based Quantum Dots via a “Bottom-Up” Approach: Topology, Chirality, and Free Radical Processes in “Building Blocks”. **Small**, p. 2205957, 2023.

ZENG, Z. et al. Graphene quantum dots (GQDs) and its derivatives for multifarious photocatalysis and photoelectrocatalysis. **Catalysis Today**, v. 315, n. December 2017, p. 171–183, 2018.

ZHU, L. et al. Lignin-based fluorescence-switchable graphene quantum dots for Fe3+ and ascorbic acid detection. **International Journal of Biological Macromolecules**, v. 194, p. 254–263, 1 jan. 2022.