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Carbon quantum dots from chitosan: main synthesis pathways and applications[1]

Quantum carbon points from chitosan: main synthesis ways and applications

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Summary

Carbon quantum dots are a new class of fluorescent nanomaterials , with properties such as photoluminescence, high solubility, low toxicity and favorable biocompatibility. They are useful for applications in biomedicine, sensors, solar cells and photocatalysis , among others. The synthesis of quantum dots using chitosan as a starting source becomes the focus of interest for researchers due to the low cost and large-scale availability of this material. Another positive point of using chitosan is the possibility of reusing natural resources with the potential to reduce pollutants and their environmental impacts. From the point of view of synthesis methods, the hydrothermal method stands out, as it is a simple and low-cost methodology, which uses moderate temperature conditions and relatively short synthesis time. Among the main applications of chitosan-based quantum dots, bioimaging and biosensors applications are the most reported in the literature.

Abstract

Carbon dots are a new class of fluorescent nanomaterials, with properties such as photoluminescence, high solubility, low toxicity, and favorable biocompatibility. They are useful for applications in biomedicine, sensors, solar cells, and photocatalysis, among others. The synthesis of quantum dots using chitosan as a starting source becomes the focus of interest for researchers due to the low cost and large-scale availability of this material. Another positive aspect of using chitosan is the possibility of reusing natural resources with the potential to reduce pollutants and their environmental impacts. As regards the synthesis methods, the hydrothermal method stands out, as it is a simple and low-cost methodology, which uses moderate temperature conditions and relatively low synthesis time. Among the main applications of chitosan-based quantum dots, applications of bioimaging and biosensors are the most reported in the literature.

Introduction

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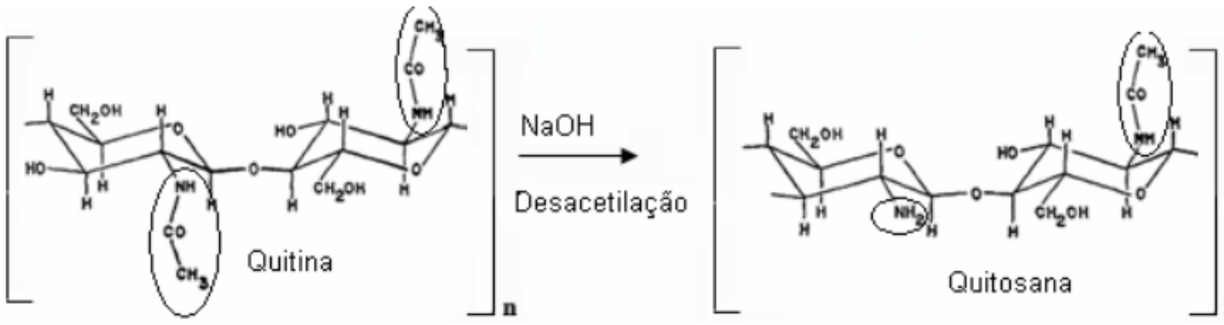
Chitosan is a low-cost, renewable and biodegradable biopolymer of animal origin of great economic and environmental importance. It has a chemical structure similar to cellulose vegetable fiber and chitin biopolymer , differing from these by their functional groups. Hydroxyl groups (OH) are arranged in the general carbohydrate structure for cellulose and amino groups (NH_2) for chitosan (Fig. 1). It is soluble in diluted acidic medium, forming a cationic polymer, with the protonation of the amino group (NH_3^+), which confers special properties differentiated in relation to vegetable fibers (Dutta, Duta & Tripathi, 2004) .

Figure 1 – Chitin deacetylation process and obtaining chitosan.



Source: (Abreu, 2008) .

The main source of occurrence of chitosan is the shell of crustaceans, which is normally discarded by the industry, becoming a potentially polluting residue, therefore, the use of chitosan reduces the environmental impact caused by the accumulation and storage in the places where it is produced (Azevedo et al . ., 2007)

Due to its constitution containing a high amount of amino ($-NH_2$) and hydroxyl (-OH) functional groups, a new possibility of application of chitosan is as a starting material in the synthesis of carbon quantum dots (Janus et al., 2019 ; Kandra & Bajpai, 2020) . The materials synthesized from chitosan have biocompatibility and non-toxic properties (NV; Kumar, 2000; Rinaudo, 2006) .

Carbon quantum dots (CQPs) are nanoparticles, with sizes up to 10 nanometers, which basically consist of sp^2/sp^3 carbon nuclei and groups containing oxygen and nitrogen or polymeric aggregations in their structure (Liu, Ye & Mao, 2007) . The chemical composition of PQCs depends on the carbon precursor used, as well as the preparation conditions (Kwon, Do & Rhee, 2012)

Carbon quantum dots (PQCs) or carbon quantum dots (C-dots) were accidentally discovered in 2004, in the electrophoresis process of single-walled carbon nanotubes (Xu et al., 2004) . PQCs have attracted a lot of attention due to their easy obtainment and fascinating properties (Peter Mirtchev, et al., 2012) .

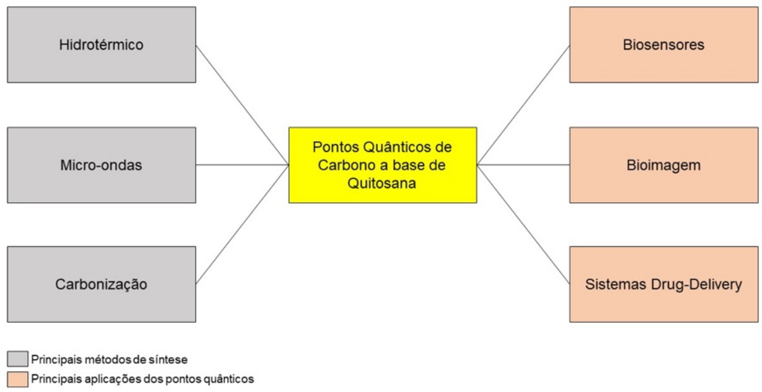
This new class of carbon materials has been gaining attention from researchers due to the extension of technological applications from this material, for example: sensors, photocatalysis , bioimaging , controlled drug release systems, solar cells, and light emitting diodes (LEDs) (Gong et al., 2019; LI et al., 2018) .

1. QUANTUM DOTS BASED ON CHITOSAN: STATE OF THE ART

Chitosan appears as an important precursor source in the synthesis of carbon quantum dots. This nanomaterial can be obtained by several synthetic routes and its range of applications makes this class of carbon fluorescent materials increasingly important (Fig. 2).

Figure 2 – Main ways of synthesizing and applying chitosan-based carbon quantum dots.

Among the advantages of using this type of nanomaterial are photostability , favorable biocompatibility, low toxicity, solubility, high sensitivity and excellent selectivity to target analytes. In addition to the advantages mentioned above, the use of natural sources as raw material allows for milder synthesis conditions,



sometimes dispensing with further separation and purification steps.

2.1. *Quantum Dot Synthesis Methods*

As for obtaining carbon quantum dots, several synthetic methods can be used. The development of more adequate synthesis methods is an important step to enhance the applications. Among these include the destruction of graphite or carbon materials into nanometer-sized graphite particles by means of physical or chemical methods. These methods may involve techniques such as electric arc discharge, laser ablation, electrochemical oxidation, chemical oxidation, and microwave-assisted processes (Zhang et al., 2018) .

Synthesis methods can be subdivided into two groups, top- down and bottom-up , which differ in the synthesis strategy and also in the used precursors. In top- down methods , PQCs are prepared from larger carbon precursors such as diamond, graphite, carbon nanotubes and graphite oxide. In bottom-up approaches, PQCs are synthesized from molecular precursors, such as citric acid, glucose and resin, which can additionally be purified by means of centrifugation, dialysis, electrophoresis, or another separation technique (Machado et al., 2015) .

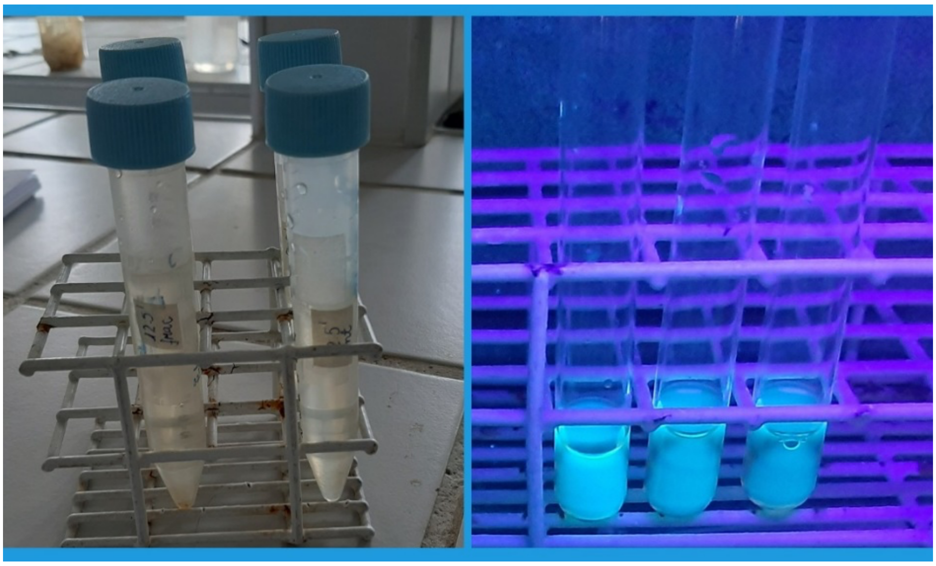
Bottom-up methods stand out in terms of particle synthesis efficiency considering the following aspects: quality, purity, cost-effectiveness and time management. Specifically, bottom-up methods allow PQCs with morphological control and better particle size distribution obtained (ZHANG et al., 2018) . On the other hand, top- down methods are more widely used for the production of PQCs from natural products (Table 1). Among the top- down methods , hydrothermal carbonization, extraction, chemical oxidation, and microwave treatment stand out (Zhang et al., 2018) .

Table 1 – Main methods of synthesis of chitosan-based carbon quantum dots.

SYNTHESIS METHOD	REFERENCES
hydrothermal	(MORADI et al., 2018)
	(BRISCOE et al., 2015)
	(GOMES et al., 2019)
	(LIN et al., 2020)
	(ZHAN et al., 2019)
microwave	(SARKAR; BOHIDAR; SOLANKI, 2018)
	(CHOWDHURY; GOGOI; MAJUMDAR, 2012)
	(KANDRA; BAJPAI, 2020)
Carbonization	(HUANG et al., 2014)
	(CHOWDHURI et al., 2016)
	(KUMAR et al., 2018)

Source: Author himself.

Figure 3 – Carbon Quantum Dots under sunlight and under ultraviolet light.



The hydrothermal method stands out for being a low-cost, environment-friendly method, however, the generation of waste is a negative point of this synthesis route. In this process, the precursor is placed in a Teflon® reactor inserted in a stainless steel beaker and subjected to heating. On the other hand, in the carbonization method, the reaction is conducted directly by heating the starting material in a muffle furnace, dispensing with specific apparatus for the reaction.

The microwave method is considered a fast method, in accordance with Green Chemistry, and has the advantages of decreasing the reaction time and dispersing particles with a more uniform size obtained by transient heating. Furthermore, the use of microwaves significantly increases the yield of high quality quantum dots (Liu et al., 2019) .

2.2 . *Properties and applications of Quantum Dots*

Carbon quantum dots are known for their physicochemical properties, namely: luminescence, low cytotoxicity, chemical inertness, low photodegradation and excellent biocompatibility (Machado et al., 2015) . They also have optical properties: photoinduced electron transfer, electrochemiluminescence (EQL), and quantum yield – characteristics that make a nanomaterial increasingly interesting for technological applications.

Due to the nitrogen present in the constitution of chitosan, the synthesized carbon quantum dots present their photoluminescent characteristics increased (Fig. 3) when compared to other types of carbon quantum dots (Moradi et al., 2018) . Furthermore, chitosan quantum dot modification can effectively improve biocompatibility and provide extra support for biomedical applications (Lin et al., 2020) .

The luminescence properties of CQDs are associated with the bandgap energy that depends on the composition of the semiconductors, as well as the size of the quantum dots (Gomes et al., 2019) , making this material promising for applications such as solar cells.

Chitosan carbon quantum dots have been used for diverse applications in biomedicine (Table 2), their applications in this field are due to low-cost and less exhaustive synthetic routes, long-term colloidal stability, elemental abundance and low environmental and biological toxicity (Baker & Baker, 2010) .

Table 2 – Main applications of chitosan-based carbon quantum dots.

APPLICATIONS	REFERENCES
Biosensors	(SARKAR; BOHIDAR; SOLANKI, 2018) (HUANG et al., 2014) (GUO et al., 2017) (CHOWDHURY; GOGOI; MAJUMDAR, 2012)
Bioimage	(MORADI et al., 2018) (LI et al., 2014) (LIANG et al., 2016)
Ion Detection	(ZHAN et al., 2019) (KUMAR et al., 2016)
Solar Cells	(GOMES et al., 2019) (BRISCOE et al., 2015)
Drug -Delivery Systems	(LIN et al., 2020) (KANDRA; BAJPAI, 2020) (CHOWDHURI et al., 2016)

Source: Author himself.

Among the applications listed in the table above, the following stand out for their innovative proposals: Cell labeling and in vivo imaging, where a new method is reported that uses chitosan as a connector to synthesize fluorescent nanocomposites from chitosan quantum dots (LI et al . , 2014) .

nanoscale organic structures , synthesis and encapsulation of the target molecule (folic acid) on the surface of chitosan-modified magnetic nanoparticles in a single step being useful for administering anticancer drugs (Chowdhuri et al. ., 2016) .

2. Conclusions

Carbon quantum dots synthesized from chitosan are gaining attention from researchers due to their variety of applications. Chitosan, as it is a biopolymer biocompatible , it increases the biocompatibility properties of carbon quantum dots, which makes this material suitable for biomedical applications, such as bioimaging and biosensor . Furthermore, due to the constitution of chitosan, carbon quantum dots show improved luminescence properties.

The hydrothermal synthesis method stands out in the literature as the most applied for synthesis because it is a relatively simple and low-cost methodology, which uses milder synthetic conditions. However, microwave-assisted methods are also a useful methodology for rapidly obtaining nanomaterials .

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