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Article

Synthesis and characterization of carbon-based quantum dots for use in biotechnology

Síntesis y caracterización de puntos cuánticos a base carbono para su uso en la biotecnología

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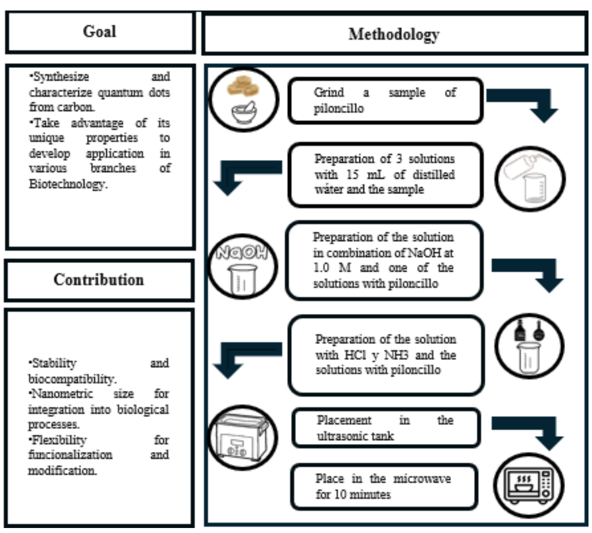
Abstract

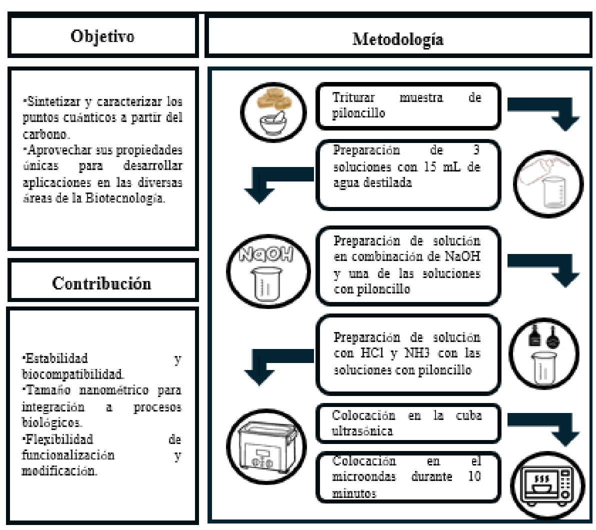
Carbon quantum dots (CQDs) are spherical nanoparticles (CNPs) with a size between 2-10 nm and a crystalline structure. They have unique properties, such as high biocompatibility and luminescence produced by their absorbance and emission of light. This shows optical properties that are not seen in larger scale materials. Due to their low toxicity, CQDs offer a versatile platform for various applications, including medical diagnosis, bioimaging, substance detection, controlled drug release, photodynamic therapy and biomarking techniques. They can be synthesized by methods such as ultrasound and microwaves, pyrolysis, hydrothermal synthesis, or exfoliation of carbon materials. Their study and development is an active area of research in biotechnology, nanotechnology and materials science. This work focuses on the properties that this type of nanoparticle has, the synthesis used for its manufacture and the possible uses as a tool in different biotechnological processes.



Synthesize, Characterization, Quantum dots

Resumen

Los puntos Cuánticos de carbono (CQDs) son nanopartículas de forma esférica (CNPs) con un tamaño entre 2-10 nm y una estructura cristalina. Cuentan con propiedades únicas, como elevada biocompatibilidad y luminiscencia producida por su absorbancia y emisión de luz. Lo que exhibe propiedades ópticas que no se observan en materiales a mayor escala. Debido a su baja toxicidad los CQDs ofrecen una plataforma versátil para diversas aplicaciones, incluyendo diagnóstico médico, bioimagen, detección de sustancias, liberación controlada de fármacos, terapia fotodinámica y técnicas de biomarcaje. Pueden ser sintetizados mediante métodos como ultrasonido y microondas, pirólisis, síntesis hidrotermal o exfoliación de materiales de carbono. Su estudio y desarrollo es un área activa de investigación en biotecnología, nanotecnología y ciencia de materiales. El presente trabajo se enfoca en las propiedades que este tipo de nanopartícula posee, la síntesis usada para su fabricación y los posibles usos como herramienta en los diferentes procesos biotecnológicos.



Síntesis, Caracterización, Puntos cuánticos

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Introduction

Quantum dots (QDs) are small semiconductor nanoparticles (NPs) of 2 to 10 nanometers (nm) in diameter. They are composed of various materials, including semiconductors, metals and carbon. They typically contain only 100,000 atoms and have a well-defined crystalline structure, allowing them to reveal unique optical and electronic properties (Tao et al., 2019).

They possess qualities such as electron confinement, energy quantization and the ability to absorb and emit light at different wavelengths depending on their composition and size. Furthermore, due to their tiny size, QDs suffer several quantum effects such as the discretization of their energy bands. Under these characteristics, QDs can interact with light and matter differently than materials on a larger scale; this is due to the quantum confinement effect, which occurs when particles are so small that electrons behave differently due to energy quantization. Quantum confinement occurs when the diameter of the crystal is smaller than its Bohr radius and influences the properties of the QDs to be quite different from those of macroscopic materials (B.H. Juárez, 2011).

An attractive property of these NPs is that they show confinement in the three directions of space; this is because the electrons are restricted to move in extremely small regions, less than 10 nm.

QDs can be considered nanocrystalline due to their crystalline structure and nanometric size; and since they are made up of semiconductor materials, they have a valence band (saturated with electrons) and a conduction band (empty energy band) separated by an energy difference called a gap.

The luminescent process in quantum dots occurs through the emission of light when electrons relax from a higher energy state to a lower energy state. This process consists of four stages, excitation, relaxation, emission and recombination. During the excitation phase, the QDs absorb the energy of incident light, which excites the electrons in the valence band and leads them to a higher energy state in the conduction band, leaving gaps in the Valence band.

When the excitation phase ends, the relaxation phase begins; in this phase the electrons in the state of higher energy are relaxed toward the lowest energy state, releasing the excess of this in the form of light generated as a radiative combination between the generated electrons and holes, causing the emission of photons with a defined energy. This gives way to the emission phase, where the emitted light has a specific wavelength, which depends on the size and composition calculated by the separation between the two energy levels. Finally, the recombination phase is reached, in which electrons and gaps recombine, releasing excess energy in the form of light (Cui et al., 2018).

The importance of knowledge of quantum dots lies in their potential to be used in a variety of biotechnological applications such as bioimaging, photodynamic therapy, drug administration, medical diagnosis, genetic applications, bioassays, biosensor development, among others. In addition to their applications, they can enhance understanding of different biological processes to develop new tools and technologies for creating smaller and more efficient devices and materials, while promoting understanding of quantum physics and its applications in engineering.

The added value of quantum dots development in the present work is the use of carbon as a basis; as it is more sustainable compared to its manufacture with other materials, as they can be produced from renewable sources of carbon. This feature makes them biocompatible and of low toxicity, without losing their chemical stability, resulting in a great resistance in aggressive environments and endowing them with a great versatility, as they can be functionalized with different chemical groups. Not to mention that its profitability is quite attractive, as it is considerably lower compared to other materials.

The present work seeks to obtain the optimal conditions for the synthesis and characterization of carbon-based QD for IR and UV-VIS tests to analyse the scope of these possess and taking that into account consider what uses could give them for their implementation in the biotechnological area.

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Background

The term quantum dots is mainly associated with nanoparticles with diameters less than 10 nm, typically based on a metal and a nonmetal (commonly group 15 or 16), which show different optical properties not only from macroscopic materials, but also from corresponding nanoparticles with sizes greater than 10 nm (Murray et al., 2000). This is due to electronic confinement (also called quantum confinement) due to the small particle size (Ashoori, 1996), which for this type of materials results in photon absorption typical in the near UV or the visible and strong emission (high quantum yield – ratio of photons emitted between those absorbed) adjustable throughout the visible range. Semiconductor quantum dots were discovered in 1980 by two independent groups, one in Russia by Alexei I. Ekimov in a glass array; and the other in the United States of America by Louis E. Brus and Alexander Afros who obtained them in colloidal solutions (Akimov & AMP; Anshchenko, 2023).

Currently, they are being researched for electro-optical applications such as photovoltaic devices (such as dyes absorbing sunlight), light-emitting diodes (already with commercial applications such as their use in QLED televisions, for example), photosensing, photocatalysis and bioimaging (as an alternative to traditional stains for fluorescent microscopy) (Bera et al., 2010; Kairdolf et al., 2013; Martynenko et al., 2017).

The range of applications for quantum dots is wide, however, there are concerns about the effect on health and the environment with the use and disposal of these materials which include metal ions such as Cd2+, Pb2+ as well as some non-metals such as As3-, Se2-, and Te2- considered toxic (Filali et al., 2020; Hardman, 2006).

From this point lies the interest in less dangerous alternatives, such as carbon-based quantum dots (CQDs). These were discovered in 2004 when researchers purified the soot residue of arc flash by synthesizing carbon nanotubes and noticed unexpected fluorescent properties (Xu et al., 2004).

Since that study to date, there has been great progress in the scientific community that seeks to replace inorganic quantum dots with carbon quantum dots that can provide similar properties with simple syntheses, at low cost, using widely available precursors, with easy waste management, lower toxicity and greater biocompatibility, for use in areas of medicine and energy mainly.

Synthesis of CQDs

The synthesis of CQDs tends to include a breakdown, polymerization, and carbonization of molecules. Normally this process occurs in some aqueous medium, so the final functional groups on the surface of CQDs are hydrophilic (Cayuela et al., 2016).

In the present paper the CQDs were synthesized using an organic precursor; piloncillo, this contains carbohydrates such as sucrose, glucose and fructose. This means that it has functional groups such as -OH and -CO; these groups can dehydrate at high temperatures, which is why it was decided to carry out this synthesis by ultrasound and microwave. This process by which synthesis is carried out is called sonication, and the type of chemistry used in this technique is known as Sonochemistry (Dong et al., 2013).

Methodology

The synthesis of quantum points of carbon was carried out using a green synthesis taking as a precursor the glucose from the piloncillo, a base of Sodium Hydroxide (NaOH), Hydrochloric Acid (HCl) and an ammonia base (NH_3), thus obtaining a homogeneous solution (Figure 1).

Box 1

Figure 1

Homogeneous solutions with piloncillo as a precursor and base of NH3 (right vessel), NaOH (medium vessel) and HCl (left vessel)

Source: Own elaboration

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The sample is crushed with the help of a mortar until a fine powder is obtained from it, subsequently 3 solutions were prepared in which they were mixed at 1.0 M of the respective powder, using this unique concentration for the 3 different solutions with 30 mL of distilled water each, consequently they were stirred to obtain a homogeneous mixture with the piloncillo respectively.

Once prepared the solutions with distilled water and the sample were subjected to the ultrasonic cube for a period of 30 minutes (Figure 2).

Box 2

Figure 2
Solutions subjected to ultrasonic cleaning

Source: Own elaboration

The solutions were subsequently prepared with NaOH, HCl and NH3. For the NaOH solution, 30 mL of distilled water and one 1.0 M solution were used, for the HCl and NH3 solution, a combination of 30 ml of distilled water and a 30% V-V solution was used, and the solutions were shaken until they were completely diluted.

To complete this process, the homogeneous mixture of piloncillo is placed in a precipitated jar and the precursor solutions are added to it (Figure 3), again the mixtures are shaken for 15 minutes, subsequently exposed for 30 minutes to the ultrasonic cube and finally subjected to microwave for 7 minutes at a power of 10 Watts.

Box 3

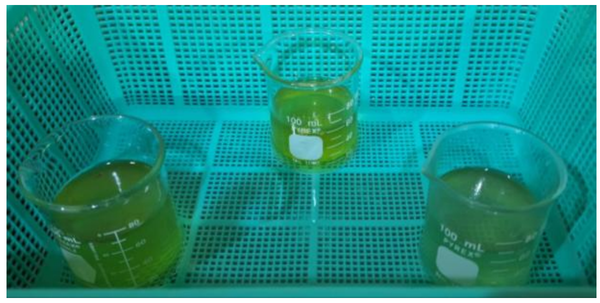

Figure 3
Precursor solution with homogenized base solution and NH3 (right vessel), NaOH (medium vessel) and HCl (left vessel)

Source: Own elaboration

Results

Box 4

Figure 4
CQDs with UV exposure

Source: Own elaboration

Uv-vis spectroscopy

The different solutions contained in the CQDs were exposed to ultraviolet light radiation, to visually check for luminescent properties. Figure 4 shows samples obtained from CQDs with and without ultraviolet radiation where the presence of luminescent properties is confirmed.

The aquatic solutions of quantum dots have their maximum excitation at 341 nm within the ultraviolet spectrum and an emission close to 442 nm inside the visible range in a cyan-blue color.

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From the spectroscopes it is observed that the intensity of luminescence depends on the increase in the concentration of organic material (Figure 5) until it reaches an over-saturation in concentration and has a decrease in intensity due to a phenomenon called cooling of concentration, on the other hand, the luminescent intensity will depend on the reaction time.

Box 5

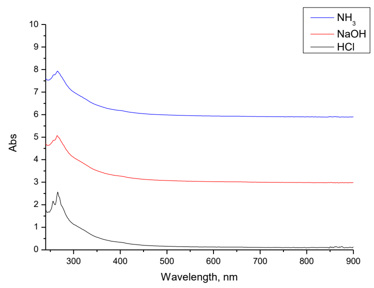

Figure 5
UV-Visible Spectrum of Quantum Carbon Dots

Source: Own elaboration

UV-Visible spectra show wide absorption at 280 nm (Figure 5) which is consistent with what is in various research (A. Mewada, 2013).

The quantum carbon dots have absorption bands at 250 and 280 nm, (Figure 2), which correspond to the bond and transition π-π* between carbon atoms C=C of aromatic domains, such absorptions are attributed to the n- π transition of the bands C=O and C = C. On the other hand, an absorption at 280 nm is observed indicating the presence of carbon nanoparticles.

FT-IR spectroscopy

Infrared spectroscopy was used to identify functional groups present in the carbon quantum points of the representative samples. IR spectroscopes (Figure 6) show absorption bands present at 3339, 2118, 1627 and 1159 at 1021 cm-1, indicating the existence of functional groups OH-, C-H, C-N, C=C and C-O, C-OH, C -O-C, COOH, C = C (Valencia, 2019).

From these results the quantum carbon dots obtained from piloncillo are composed of multiple functional groups which makes them highly soluble in water and makes them good candidates for their application in biotechnology.

Box 6

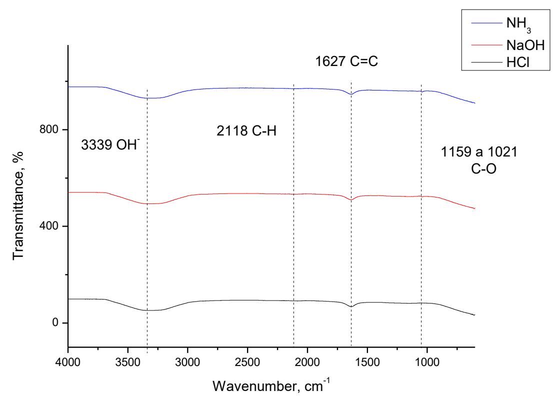

Figure 6
FT-IR spectrum of Quantum Carbon Dots

Source: Own elaboration

Another variable to which the maximum intensity is attributed is to concentration; where at lower concentrations greater intensity, because at less matter, there is greater number of interactions for the formation of quantum dots. (Metha, 2014).

Conclusion

Quantum carbon dots were synthesized, with different solvents, obtained from piloncillo, which are cost-effective for their low cost of synthesis and environmentally friendly. Optimal emission conditions were found at a concentration of 0.1M in a time of 3 hours, presenting a maximum excitation at 280 nm, which will allow surface passivation for anchoring with biomolecules for application in biotechnology.

According to the FTIR analysis, the functional groups OH-, C-H, C-N, C = C and C-O, C - OH, C – O-C, COOH, C=C are identified as responsible for the functionalization of the surface that allowed the obtaining of luminescent properties (blue emission when excited by ultraviolet light with a wavelength of 254 nm).

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Declarations

Conflict of interest

The authors declare no interest conflict. They have no known competing financial interests or personal relationships that could have appeared to influence the article reported in this article.

Authors' Contribution

The contribution of each researcher in each of the points developed in this research, was defined based on:

Granados-Olvera, Jorge Alberto: Contributed to the project conception, research method and synthesis. He performed the analysis of results and the characterization of quantum dots, as well as the writing of the article.

Calvillo-Beltrán, Sofía Valentina: Conducted the synthesis of quantum dots and collaborated in the development of graphs for the evaluation of results. She also contributed to the drafting of the article.

Arroyo-Ordoñez, Ivan: Contributed to the development of the research and the introduction, the type of quantum dots and the results collection. He also helps with the approached and the writing of the article.

Rangel-Ruíz, Karelia Liliana: Worked on the search for applications of quantum dots in the biotechnology area and on data collection. She also collaborated in the writing of the document.

Availability of data and materials

The availability of materials is quite wide, and they are in the industrial category due to since the precursor, in this case piloncillo, can be easily obtained in different grocery stores. The equipment used for the Sonochemical technique is inexpensive compared to other methods and gives optimal results. The data, on the other hand, were obtained from the spectra and graphed with a program.

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Abbreviations

CNPs: Core-Shell Nanoparticles

CQDs: Carbon Quantum Dots

nm: Nanometer

NPs: Nanoparticles

QDs: Quantum Dots

UV-vis: Visible ultraviolet

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Antecedents

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