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Synthesis of Carbon Quantum Dots Through Electrochemical Exfoliation and Their Potential for Biomedical Use

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ABSTRACT

Carbon quantum dots are a new class of zero-dimensional carbon nanomaterials that due to their low toxicity, high water dispersibility and fluorescent properties, have attracted o lot of attention for biomedical applications. They can be synthesized with many different methods through both bottom-up and top-down approaches. In this mini review we summarize the existing literature regarding the electrochemical exfoliation of pure graphite that produces nanostructures of diameter smaller than 10 nm. We focus on the electrolytes that are used and the voltage applied, as the main factors that contribute on the size, structure, composition and yield of the carbon quantum dots. In order to explain the findings of the literature, we briefly analyze the mechanism of the graphite exfoliation from the ions, under applied voltage. Furthermore, we report on the many advantages that the electrochemical approach has over competing methodologies, that make it an attractive method for mass production of carbon quantum dots, with the intention to be used in biomedical applications.

Keywords: Carbon Quantum Dots (CQDs); Graphene Quantum Dots (GQDs); Electrochemical Exfoliation; Graphite; Biomedical Applications; Nanostructures; Zero-Dimensional Nanomaterials; Fluorescence

Abbreviation: CQDs: Carbon Quantum Dots; GQDs: Graphene Quantum Dots; CDs: Carbon Dots; GO: Graphene Oxide; CNTs: Carbon Nanotubes; NTUA: National Technical University of Athens

Introduction

During the last few decades, nanocomposites have attracted considerable scientific interest in terms of biomedical applications, such as molecular imaging, biosensors, targeted drug delivery, wound healing, photodynamic therapy and bio-engineering applications [1,2]. Recently, carbon-based nanostructures, especially carbon quantum dots (CQDs), have gained intense attention for such applications owing to their unique and novel properties, as good biocompatibility, good cell permeability, low cytotoxicity, excellent dispersibility in water, flexibility in surface modification, chemical inertness and good optical performance [3]. Carbon quantum dots (CQDs), also known as carbon dots (CDs) or graphene quantum dots (GQDs), comprise a zero-dimensional nanomaterial, characterized by chemical structure and physical properties similar to those of graphene oxide (GO), thus

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differentiating in terms of size, being quasi-spherical nanoparticles with a diameter less than 10 nm [2]. Up to nowadays, numerous approaches for synthesizing CQDs have been proposed, including laser ablation, chemical ablation, arc discharge method, incomplete combustion of carbon soot, microwave synthesis, carbonizing polymerized resols on silica spheres, hydrothermal method, organic carbonization, thermal oxidation of suitable molecular precursors, proton-beam irradiation of nanodiamonds and dehydration of carbohydrates.

However, the vast majority of the aforementioned methods require relatively complex procedures, as well as strict conditions that may have adverse effects on the final product, such as poor crystallinity, impurities, intricate post-treatments and limited physical and chemical properties [4,5]. Electrochemical methods have begun to be acutely explored for the synthesis of CQDs, due to several benefits, as simple apparatus, easy post-treatment and purification methods, high yield, good reproducibility, and low cost [4,5]. Various materials can be utilized as electrodes during the electrochemical preparation of carbon quantum dots, as graphite rods, carbon nanotubes (CNTs), carbon paste, carbon fiber and Pt sheets with the carbon source within the electrolytic solution [4]. Both the electrolytic solutions and the electrode materials play a vital part in the synthetic procedure, leading to the development of CQDs with different properties, related to surface states, cytotoxicity and photoluminescence (PL) performance [4]. Within the framework of this short review, we offer valuable insights into the electrochemical fabrication of carbon quantum dots through one-step exfoliation of graphite rods, since it constitutes a facile, fast and low-cost method, which produces CQDs with desirable properties for biomedical applications.

Electrochemical Exfoliation of CQDs/GQDs

In 2012, Ming and co-workers [5], reported a one-step electrochemical approach for the synthesis of high-quality and photocatalytically active CQDs utilizing additive-free ultrapure water in the reaction system and high-purity graphite rods, both as anode and counter electrode. Also in 2012, Zhang, et al. [6], fabricated water-soluble and uniform-sized graphene quantum dots (GQDs) through the electrochemical exfoliation of a graphite rod (anode) in an alkaline electrolyte (0.1 M NaOH aqueous solution), followed by room temperature reduction with hydrazine. The as-prepared GQDs were characterized by strong yellow luminescence with a 14% quantum yield, while they had the ability to penetrate into stem cells, presenting no affection to their viability, proliferation or differentiation capacity. The research team concluded that such fluorescent GQDs constitute excellent candidates for several biomedical applications, as tracking proliferation, apoptosis and differentiation of various cell lines and drug delivery. Tan, et al. [7], have reported the synthesis of GQDs characterized by uniform size (~3 nm), solubility in water, as well as red emission. The synthetic procedure included the electrochemical exfoliation of graphite rods in K2S2O8 aqueous solution. The as-prepared GQDs indicated good photostability and reduced cytotoxicity, rendering them suitable for several biomedical applications.

Liu and his co-researchers [4], fabricated monodisperse, high-crystallinity and luminescent CQDs through exfoliating electrochemically a graphite electrode using an alkaline electrolyte. Then, the team examined the applicability of the as-synthesized CQDs in cell imaging, proving they could constitute an excellent fluorescent bio-imaging agent, due to their good biocompatibility and low cytotoxicity. Muthurasu, et al. [8], reported the development of water soluble and fluorescent graphene quantum dots (GQDs) utilizing a constant current electrolytic exfoliation of a graphite rod in an aqueous or alkaline solution, containing sodium methoxide as the electrolyte. The team reported that the GQDs presented good biocompatibility and low cytotoxicity. During 2017, Ahirwar, et al. [9] developed graphene quantum dots (GQDs) and graphene oxide quantum dots (GOQDs), through an electrochemical exfoliation technique with high-purity graphite rods as electrodes (anode and cathode), an aqueous solution of citric acid and alkali-hydroxide acting as the electrolyte and a constant potential applied (+10V). GQDs and GOQDs indicated blue to green fluorescence below 365 nm UV irradiation, rendering them promising candidates for several applications. Joseph and Anappara, also in 2017 [3], utilizing a two-electrode cell apparatus, consisting of graphite rods as electrodes and an aqueous mixture of NaOH/urea/H2O2 as electrolyte, synthesized white-light emitting CQDs.

In 2018, Devi and his co-researchers [10], also adopted a simple electrochemical method for fabricating CQDs, using graphite rods as anode and cathode and 0.1M NaOH/ethanol as electrolyte solution. The CQDs presented strong green fluorescence under UV irradiation. Afterwards, in 2019, Fu, et al. [11] confirmed the development of N-GQDs, suitable for bio-imaging applications, as they were characterized by desirable physico-chemical properties. The aforementioned fluorescent N-GQDs were prepared electrochemically via exfoliation and oxidation of graphite rods in an aqueous NaOH/semicarbazide electrolyte under a constant voltage equal to 5V. Lastly, in 2021, another research team [12], utilized a one-step electrochemical exfoliation method for developing fluorescent GQDs. More specifically, graphitic rods deriving from dry batteries, were used as electrodes, while the electrolytic solution was a mixture of citric acid (0.1M) and NaOH (1M). Also in 2021, Danial, et al. [13], successfully prepared GQDs with an average size equal to 5 nm approximately, by exfoliating electrochemically graphite rods, using an aqueous electrolyte solution of citric acid and NaOH.

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Mechanism of the Electrochemical Exfoliation, Benefits and Limitation

The mechanism of the electrochemical synthesis of carbon quantum dots is based on the intercalation of ions in the graphite defects and the exfoliation of nanosized flakes. The ions attack the graphite structure under the influence of the applied voltage [14]. If only one graphitic electrode is used, the exfoliation will be anodic or cathodic depending on whether the electrode will be used as anode or cathode accordingly. In anodic exfoliation, the prosses is based on the anions of the electrolyte, like the hydroxyl ions that already exist on the electrolyte (with the addition of NaOH for example) or they are created through the electrolysis of water. If the graphite is used as the cathode, then the prosses is based on the cations of the electrolyte. Research suggests that the anodic exfoliation is more efficient even though it results in the production of more defects and oxidative species on the product [15]. In both cases however, energy is wasted on the counter electrode that is used. A way to solve this drawback is the use of graphite electrodes as both the anode and cathode [16]. Electrochemical exfoliation of graphite has a number of advantages over the other methods of producing carbon quantum dots. It is a simple prosses that requires cheap and easy to use equipment. Furthermore, it can be scaled up easily, providing an economically viable method for the production of carbon dots that has potential to close the gap between laboratory-scale synthesis and industrial production [17].

Compared to other methods, the electrochemical exfoliation avoids extreme reaction conditions, like toxic chemicals or high temperatures, thus making it a greener alternative which is an important factor in current research goals [18,19]. Also, this method produces quantum dots with good crystallization, which is a common problem reported with a lot of bottom-up approaches [18,20,21]. However, there are some drawbacks with the electrochemical exfoliation, that need to be addressed. The yield of carbon quantum dots is generally low due to the fact that during the intercalation of the ions in the graphite, larger parts of graphene particles are created, that are not exfoliated further [4,5]. Also, the production of carbon dots slows as time passes due to the fact that ion species accumulate on the sites [22].

Conclusion

In conclusion, carbon quantum dots are a new type of carbon nanomaterial with a lot of potential in biomedical applications, such as bioimaging, biosensors and photodynamic therapy. A lot of different methods of synthesis have been reported, including bottom-up and top-down approaches each with a number of drawbacks such as expensive equipment, use of toxic chemicals or high energy requirements, that need to be addressed. Electrochemical exfoliation of graphite is a wet chemical prosses that has attracted research interest due to its controllability, scalability and feasibility, while requiring cheap equipment and also represents a greener approach compared to the other methods. The type of the electrolyte and the applied voltage are important factors to consider, which can be explained be the mechanism of the exfoliation. Of course, there are some disadvantages that lower the yield of carbon quantum dots. Despite that, the electrochemical method remains a viable approach for the synthesis of carbon quantum dots.

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Conflict of Interest

The authors declare no conflict of interest.

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