# Synthesis of Carbon Quantum Dots Based on Hydrothermal Method and Its Application

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**Abstract.** Recently, carbon quantum dots (CQDs), one of the newest “zero-dimensional” carbon-based materials, have attracted extensive attention from a wide range of researchers and scholars both at home and abroad. This is attributable to their special optical properties, photo-stability, biocompatibility, water solubility and low toxicity, which allow them to be used effectively in a variety of applications. As a result, various methods have been spawned to synthesize a diverse of different CQDs. Among all the synthesis methods, hydrothermal method is favored by the majority of researchers due to its controllable reaction conditions, low reaction energy consumption and high product yield. This paper will summarize the characteristics and principles of the hydrothermal synthesis method. On this basis, the paper further discusses the role of hydrothermal synthesis methods in modulating the fluorescence efficiency and surface structure of CQDs, and focuses on the use of CQDs for anti-counterfeiting materials, bioimaging, fluorescent sensors and electrode materials. Finally, this paper presents the problems in their development process and gives an outlook on their application prospects.

**Keywords:** Carbon quantum dots, Hydrothermal Synthesis, Mechanism, Application.

## 1. Introduction

Carbon-based materials perform a very valuable function in the development of science and technology. Among these, carbon-based nanomaterials such as fullerenes, one-dimensional carbon nanotubes, graphene, etc. They have excellent electrical conductivity, stable chemical properties and better biocompatibility, making them widely used in a variety of fields. However, due to the poor water solubility of carbon nanomaterials, their high fabrication cost, and the fact that they are not effective optical emitters (particularly in the visible region). This makes them limited in many applications.

Carbon quantum dots (CQDs), a novel carbon-based nanomaterial with carbon as the backbone, have been attracting attention from researchers in recent years [1]. In 2004, CQDs were discovered by chance as a by-product in an electrochemical purification process of monolayer carbon nanotubes prepared by the arc discharge method. Since then, people have used arc discharge, microwave pyrolysis, hydrothermal and other methods to synthesize CQDs, and passivated or functionalized its surface, so that CQDs can obtain many excellent properties. Compared with traditional nanomaterials, CQDs not only have similar luminescent characteristics and nanosized characteristics to traditional nanomaterials, but also have better chemical inertness, water solubility, high light bleaching resistance, easy functionalization and good biocompatibility.

Traditional CQDs need to use a lot of toxic reagents in the preparation process, such as cadmium selenide, pyridine and pyrrole, which does not meet the requirements of environmental friendliness. At present, there are many methods to synthesize CQDs. For example, Peng et al. have successfully prepared phosphorus and sulfur co-doped CQDs [2], and the obtained CQDs were uniform in size and well dispersed, with significantly improved electrochemiluminescence (ECL) performance compared to single element doping. However, these methods have some disadvantages in the process of preparing CQDs, such as complicated synthesis process, high cost, low CQDs yield and poor fluorescence performance. In contrast, the use of hydrothermal method to prepare CQDs has the advantages of cheaper instrumentation, simpler synthesis process and higher quantum yield. Therefore, in search of efficient and green industrial production methods, researchers are more likely to use hydrothermal methods as well as green raw materials to conduct research on CQDs synthesis. The use of green natural products, which enable the selection of green precursors at the source, plays a very valuable role to synthesize green CQDs and expand the multifaceted applications of biomass. Tan et al. have prepared carbon quantum dots with excellent fluorescence properties by hydrothermal method with 77.8% yield using citric acid and diethylenetriamine as raw materials [3]. Wang et al. used durian fruit pulp as a raw material to synthesize CQDs [4], with a high yield of 79% of CQDs, low toxicity and good biocompatibility. And the solutions of such prepared CQDs also exhibit various fluorescence effects.

Therefore, this paper presents a systematic analysis of the research progress of hydrothermal method for the synthesis of CQDs, mainly including the characteristics and principles of hydrothermal method, the performance regulation and application of these CQDs, expecting to provide some valuable references for scholars engaged in the research of CQDs.

## 2. Synthesis of CQDs based on hydrothermal method

### 2.1. Principles of hydrothermal method

Hydrothermal method means that in a special sealed reaction vessel, where water solution is the main reaction system. By continuously pressurizing and heating the reaction system, a high-pressure and high-temperature reaction environment can be obtained compared with the outside world, so that substances which are usually insoluble or insoluble under normal environmental conditions can be dissolved and reacted. The specific principle of the hydrothermal method is that the chemical reaction for the preparation of nanomaterials by the hydrothermal method is carried out in a high-pressure closed system containing a liquid. When the system is at a high temperature, the solute expands dramatically inside the closed vessel and rapidly fills up the entire vessel, thus generating a high pressure. The precursors commonly used in hydrothermal reactions are generally oxides or hydroxides, and when heated, their solubility gradually increases with increasing temperature, which in turn allows the solution to be supersaturated and gradually begin to form a more stable new phase of the oxide. The solubility difference between the precursors, intermediates and stable oxides, which can eventually be solvents, is the driving force for the whole reaction process.

The products prepared by hydrothermal method have the following characteristics: small particle size, uniform distribution, light agglomeration, eliminating the use of high temperature calcination and ball milling process, effectively avoiding the introduction of impurities and structural defects. The main reasons for the use of hydrothermal method are: (1) The whole process of the reaction is carried out in a closed environment, which can control the atmosphere of the reaction and facilitate the synthesis of toxic systems and minimize the pollution to the environment. (2) The target products can be effectively synthesized by changing the reaction temperature, pressure and composition of the solution. (3) Using medium temperature liquid phase control, the energy consumption of the reaction is low, and the scope of application is wide. (4) The reaction is carried out in rapid liquid-phase convection throughout, and the products obtained have high yields, good dispersion and high purity.

### 2.2. Synthesis of CQDs

Changing the chemical reaction temperature and reaction time has an important influence on the synthesis of CQDs. Wang et al. firstly pretreated VulcanXC-72 carbon black with concentrated nitric acid [5], then mixed it with sodium hydroxide, and successfully prepared CQDs by one-step hydrothermal method. After quinine sulfate solution was used as the reference solution, it was found that CQDs could be prepared at 150 °C-180 °C for a certain time by changing the reaction temperature and time. As the temperature increases, the corresponding reaction time decreases, which in turn leads to a decrease in the particle size of the synthesized CQDS. When the reaction temperature is 180 ℃ and the reaction time is 10 h, the synthesized CQDs has high quantum yield.

Wei Jie used South American white shrimp and ultrapure water as raw materials and synthesized CQDs successfully through a single-step hydrothermal method [6], and then filtered the reaction solution with an inorganic filter membrane having a specific pore size of 0.02 μm and treated the reaction solution with osmosis to obtain pure N-CQDs. The data of as-prepared N-CQDs were analyzed by fluorescence chromatography. The peak of phosphor excitation spectrum is located at 382.5 nm, and the most intense peak is located at 450 nm with a half-peak width of 59 nm. They also tested the prepared N-CQDs solid powders by UV-Vis absorption spectroscopy, as showed in Figure 1. From the graph, it is observed that N-CQDs have obvious absorption at 1000 nm~200 nm, and the absorption increases with decreasing wavelength. From the figure, it can be concluded that N-CQDs can use not only ultraviolet light but also sunlight including visible light.

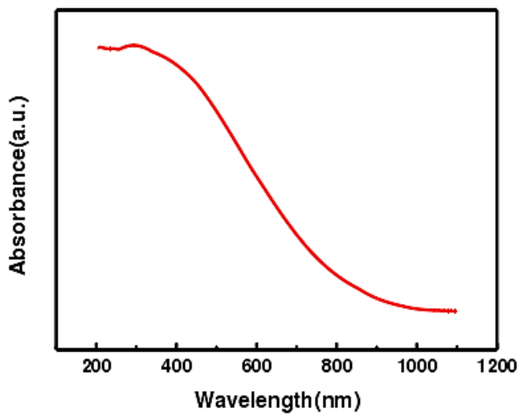


**Figure 1.** UV-Vis absorption spectrum of the prepared CQDs [6]

## 3. Application of the CQDs

As a new carbon-based material, CQDs not only have good water solubility, stability and biocompatibility, but also have excellent luminescence properties, unique fluorescence performance, good optical stability, easy functionalization and simple synthesis process, which makes it have a good application prospect in many fields such as anti-counterfeiting materials, fluorescence sensors, biological imaging and electrode materials.

### 3.1. Anti-counterfeiting materials

Along with the continuous development of productivity and the spontaneity of the market, some counterfeit products gradually appear in the public view. In response to this phenomenon, we need to study a specific anti-counterfeiting technology to prevent and stop the counterfeiting behavior. Currently, organic dyes, luminescent nanomaterials, fluorescent inks and many other materials are made and applied in anti-counterfeiting products. However, these materials are often tedious to prepare, have high toxicity, are expensive and have poor stability. Therefore, it is especially important to prepare a stable, green and non-toxic anti-counterfeiting material for the present time.

Farshbaf et al. synthesized a yellow-green fluorescent NB-CQDs using 2-hydroxyphenylboronic acid and ethylenediamine through a one-step hydrothermal method [7]. This NB-CQDs has good biocompatibility and good stability in water. The NB-CQDs have been applied to writing ink materials and can display unique colors under UV fluorescent light for easy identification of their authenticity. This fully proves their application value in anti-counterfeiting. Chen et al. prepared CQDs with good water solubility by using chitosan as raw material [8], and when the mass concentration of chitosan was 10 g/L, the temperature at 180 °C, and the time was 12 h, the prepared CQDs were structurally intact with high yields. And there were absorption peaks at 293 and 330 nm, showing blue fluorescence.

After configuring it into ink, combined with inkjet printing, it can effectively realize the encryption of information under both natural light and UV light with good anti-counterfeiting effect. Lin et al. developed an m-CQDs-PAV composite that can display all three emission modes of RTP, PL, and UCPL simultaneously [9], is difficult to replicate, and is stable enough to be directly applied to highly stable anti-counterfeiting fluorescent inks and also to many advanced anti-counterfeiting materials. Therefore, CQDs can be used as an ideal anti-counterfeiting material. Figure 2 shows the preparation of m-CQDs-PAV composites and their applications in anti-counterfeiting, respectively.

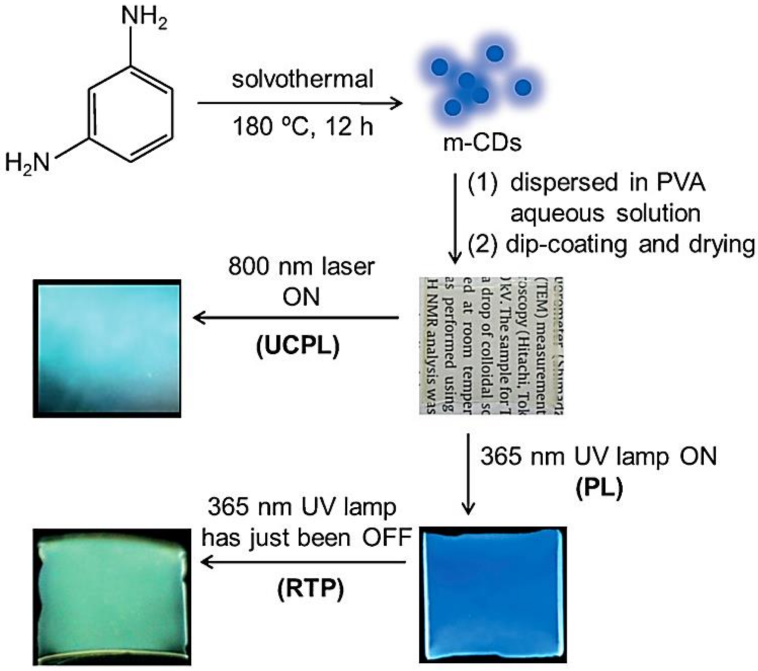


**Figure 2.** Application of the m-CQDs-PAV composites in anti-counterfeiting [9]

### 3.2. Fluorescence sensors

The electrical properties of CQDs and their associated fluorescence burst method, fluorescence sensitization method, and fluorescence resonance energy conversion method have a broad spectrum of applications in sensors. And the fluorescence spectrometer is easy and simple to operate and highly accurate, and this series of advantages have attracted the research interest of a wide range of scholars.

Lu et al. synthesized CQDs with good water solubility by a single-step hydrothermal approach using grapefruit peel as raw material [10]. CQDs have a very good selective detection function, and with a detection limit of 0.23 nmol/L for $Hg^{2+}$. The approach is now being used to test lake water samples. Lee et al. [11] constructed a fluorescent probe capable of highly accurate detection of aluminum ions using CQDs with Romindan 6G, which is currently applied in other aspects of detection such as food. Hong et al. [12] successfully prepared F-CQDs with bright blue fluorescence by using perfluorooctane sulfonic acid and hydrogen peroxide as reactants, and the fluorescence of F-CQDs suddenly disappeared when F-CQDs were mixed with $Fe^{3+}$. As shown in Figure 3, the results showed that the developed sensing method based on the prepared CQDs has high sensitivity for the detection of $Fe^{3+}$, where the detection limit is 10 nM.

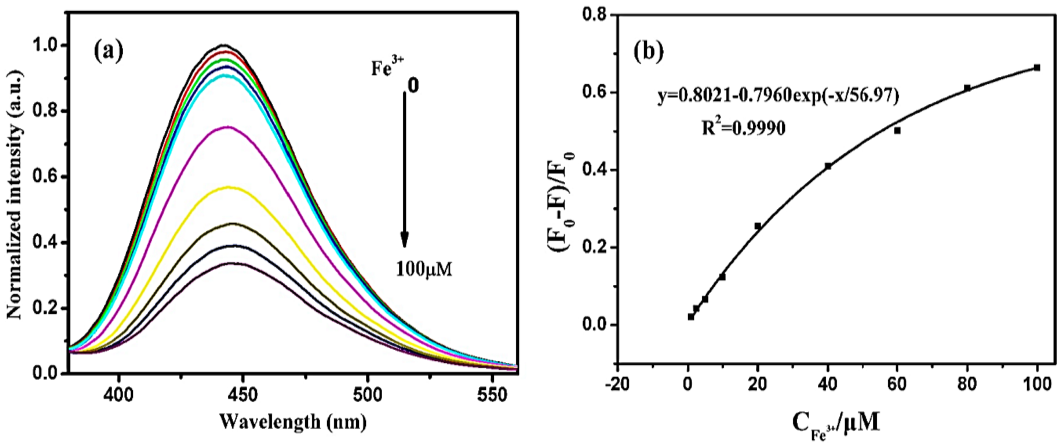


**Figure 3.** The use of the prepared CQDs for detection of $Fe^{3+}$ [12]

### 3.3. Bioimaging

Biological imaging has laid the foundation of cell biology and developmental biology research [13]. Although organic dyes, luminescent nanomaterials and various luminescent substances have been widely used in bio-imaging, these materials have poor light stability, high toxicity and poor biocompatibility, so they can't be well used in medicine. As new nanomaterial-CQDs, first of all, because the raw materials used in the synthesis of CQDs are green and environmentally friendly, it has low toxicity and low side effects. Secondly, the CQDs synthesized with a one-step hydrothermal approach have good fluorescence stability and biocompatibility. Furthermore, CQDs has continuous emission spectrum, so it can better explore deep tissue cells.

Wu et al. synthesized nitrogen-doped CQDs by a single-step hydrothermal process using tetraphenylporphyrin and metal complexes as raw materials, respectively [14]. The CQDs could be used to detect HeLa cells, and three different colors of fluorescence were observed to be excited at three different wavelengths of light during the detection process. When CQDs enter the organism, the fluorescence is mainly presented on the cytoplasm, while that present in the nucleus is very weak, so most scholars believe that CQDs enter the cell for cell imaging through endocytosis. Che prepared carbon quantum dots of 4 nm particle size, good dispersion, excellent and stable fluorescence properties [15], enriched surface functional groups, and high biocompatibility by a one-step hydrothermal synthesis using o-phenylenediamine as a precursor. The long-range tracing effect of carbon quantum dots on cell fluorescence imaging was investigated by using multi-algebraic fluorescence tracking. The experimental results show that carbon quantum dots can enter cells, distribute in cytoplasm and nucleus, exhibit stable fluorescent labeling intensity, and have great potential for rapid and selective bioimaging. Yang et al. [16] successfully synthesized M-CQDs with particle size of 5 nm by hydrothermal method with mangosteen paddle as precursor. After co-culture of M-CQDs with yeast cells for 1 h, the cells displayed an intense blue fluorescence, which indicated that M-CQDs could easily penetrate into the yeast cells. After mixing $Fe^{3+}$ with fluorescently labeled cells, the fluorescence of the cells was sharply quenched. It indicated that the M-CQDs had the potential of biological imaging in yeast cells. A schematic representation of M-CQDs for $Fe^{3+}$ ion detection and cell imaging is presented in Figure 4.

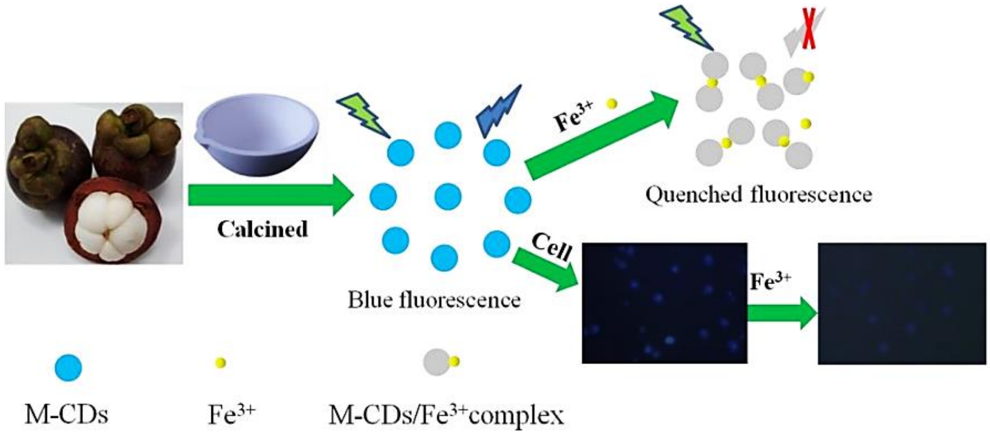


**Figure 4.** The detection of $Fe^{3+}$ ions by M-CQDs and application to cell imaging [16]

### 3.4. Electrode materials

CQDs have some properties that graphite, conventional nanomaterials, etc. do not possess: they have a good electrochemical signal and high fluorescence properties. Therefore, these two properties can be exploited to make CQDs have a great variety of applications, such as electrochemiluminescence analysis.

Liuet al. [17] successfully synthesized CQDs/graphene/cotton fabric flexible electrodes by a two-step hydrothermal method. The electrode successfully exhibited the reserve mechanism of the bilayer capacitance. The best reserve effect of the obtained electrode was achieved at a hydrothermal reaction temperature of 130 °C with a graphene addition of 0.1 g. The electrode was subjected to 1000 cycles with a capacitance retention of 72%, and it was folded repeatedly with little or no effect. Shen et al. synthesized B-doped CQDs in 54% yield by a single-step hydrothermal approach using ethylenediamine and boric acid as raw materials [18]. The B-CDs-LEDs prepared using these CQDs emitted fluorescence with a brightness of 250 cd-cm -2 at an operating voltage of 3.2 V and could be maintained continuously for more than one day. Sun et al. prepared WLEDs with color rendering index up to 93 by mixing high yield and high fluorescence blue CQDs phosphors and red and yellow copper indium zinc sulfur phosphors in combination with UV LED chips, an index much higher than that of commercial WLEDs using yellow rare earth phosphors [19]. Based on this, they later prepared WLEDs by mixing blue CQDs phosphors, yellow as well as red polymer dot fluorescence to prepare 2805-7786 K color temperature tunable WLEDs [20].

## 4. Conclusions

This paper summarizes the characteristics and principles of hydrothermal method, and then analyzes the effects of changing the reaction temperature and time on the yield and grain size of CQDs, as well as the effects of doping elements on the fluorescence properties of CQDs. Finally, the applications of CQDs in anti-counterfeiting materials, bioimaging, fluorescent sensors and electrode materials are mainly introduced.

CQDs is a kind of luminescent material that attracts more attention among emerging nanomaterials. Compared with quantum dots reported in the traditional way, CQDS has better luminescent properties, biocompatibility, low toxicity, light stability and other advantages. In addition to the above-mentioned application areas of CQDs, CQDs are widely used in drug delivery, fuel cells, photocatalysis, and many other fields. At present, biomass-based materials are the ideal materials for green synthesis of CQDs, including natural polysaccharides, cellulose, various fruits and so on. However, at present, most of CQDs synthesized from biomass-based materials are mainly blue and green, and there is a serious lack of red and yellow light, this severely limits the application of biomass-based carbon quantum dots, so the fluorescence efficiency and quantum yield of CQDs still need to be improved. On the other hand, because CQDs synthesized from biomass raw materials have diversified functional group structures and good biocompatibility, it is expected to expand the application of biomass-based carbon dots and give full play to its advantages in structure and properties. In the future, developing green, simple and efficient CQDs, and how to better play the role of CQDs' own properties and its functional group structure are very valuable research topics. CQDs has infinite application potential and development prospects. It believes that in the near future, we can explore other application values of CQDs and apply them to practical engineering applications.

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