Green preparation and application of carbon quantum dots

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Abstract: Carbon quantum dots (CQDs) are a new type of carbon-based zero-dimensional materials. Carbon quantum dots have many advantages such as excellent optical properties, good water solubility, low toxicity, environmental friendliness, wide source of raw materials, low cost, and good biocompatibility. Since the first discovery of carbon quantum dots, a variety of synthetic methods have been developed. This article lists the preparation methods and applications of carbon quantum dots, and discovers a new method for ionic liquids as modifiers, which will play an important role in the future research of carbon quantum dots.

1. Introduction
At present, the preparation of carbon quantum dots has become mature, and a series of new preparation methods have been developed. The following table lists common preparation methods and advantages and disadvantages.

| Preparation method     | Characteristics of carbon quantum dots |
|------------------------|----------------------------------------|
| Top-down approach      | The fluorescence property is good, but the yield is low |
|                        | The yield is high, but the process is complicated |
|                        | Long life of fluorescence but complex equipment |
|                        | It is easy to operate but will cause pollution |
|                        | It has polychromatic fluorescence but needs refluxing process |
|                        | Simple operation and can improve the purity |
|                        | The reaction time is short, but it cannot be produced on a large scale |
|                        | High yield but need passivation treatment |
| Bottom-up approach     | Electrochemical synthesis |
|                        | Chemical oxidation |
|                        | Combustion method |
|                        | Hydrothermal method |
|                        | Microwave synthesis |
|                        | Template method |

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1.1 background
In the history of the study of carbon quantum dots, Fullerene, a carbon nanomaterial with zero dimension, was first reported in 1985[1], then in 1991[2], one-dimensional carbon nanotubes were discovered. In 2004[3], Xu et al. Prepared single wall nanotubes by arc discharge, the luminescent nanoparticles were observed for the first time, this is also the first time that carbon quantum dots have appeared. In 2007, carbon quantum dots (CQDs) with different luminescent properties were isolated from the soot of candle combustion[5].

1.2 Properties of carbon quantum dots
The first obvious feature is that there is a strong absorption peak in the ultraviolet region. Another outstanding feature is photoluminescence. Carbon quantum dots with good water solubility will emit bright fluorescence under light. Secondly, carbon quantum dots are environmentally friendly, and heavy metals will not be used in the process of preparation. Moreover, carbon quantum dots have high biocompatibility and low cytotoxicity, and do little harm to the environment.

1.3 Top down synthesis
The "top-down" synthesis method refers to the physical or chemical stripping of large-scale carbon sources to small-scale carbon quantum dots. The carbon sources of carbon quantum dots synthesized by "top-down" method are carbon nanotubes, carbon fibers, graphite rods, carbon ash and activated carbon, these carbon rich materials were decomposed by arc discharge, laser ablation, electrochemical synthesis and other means to form carbon quantum dots.

1.3.1 arc discharge method
In 2004, Xu et al[3]. In the process of separation and preparation of single-walled carbon nanotubes by electrophoretic separation and separation, the first discovery of a fluorescent material under ultraviolet lamp irradiation is the first CQDS. Three kinds of materials with blue green light, yellow light and orange red light are found. The advantage of this carbon quantum dot is better fluorescence performance, but the disadvantage is low yield.

1.3.2 Laser ablation
The specific method is to irradiate the carbon target with a laser beam, then peel off the carbon nanoparticles from the carbon target, and then synthesize fluorescent CQDs. For example, sun et al[6]. Firstly prepared carbon targets with the mixture of graphite powder and cement by laser ablation method, using argon vapor as carrier gas, then followed by baking, curing, argon flow annealing and other processes. By attaching simple organic compounds to the acid treated carbon particles for surface passivation, the observed quantum yield increased from 4% to more than 10%.

1.3.3 electrochemical synthesis
At a certain potential, carbon nanoparticles are stripped off from the working electrode after the electrolyte is anodized. After surface passivation, carbon nanoparticles are transformed into CQDs with fluorescence properties. For example, Zhou et al[7]. Observed for the first time that carbon nanotubes were broken by cyclic applied potential to generate luminescent carbon nanotubes through electrochemical method, thus developed an efficient method of luminescent carbon nanotubes. The obtained fluorescent carbon dots were spherical, with small particle size and narrow particle size distribution, and the fluorescence quantum yield could reach 6.4%.

1.4 bottom up synthesis
The "bottom-up" synthesis method is to synthesize carbon quantum dots from small carbon materials such as molecular or ionic states. Organic small molecules or oligomers are often used as carbon sources, such as citric acid and ionic liquids. The common "bottom-up" synthesis methods include chemical oxidation, combustion, hydrothermal, microwave synthesis and template synthesis.
1.4.1 chemical oxidation method
Wu et al. [8] reported a new method to prepare water-soluble photoluminescent carbon quantum dots from petroleum coke. Firstly, petroleum coke was oxidized in the mixed solution of concentrated sulfuric acid and nitric acid, and then functionalized by hydrothermal ammonia method. After ammonia hydrothermal treatment, the quantum yield of carbon quantum dots increased from 8.7% to 15.8%.

1.4.2 combustion method
The method for the formation of fluorescent CQDs from the products of organic matter combustion after reflux acid boiling. Just like Liu [9] et al. Reported a method for efficient preparation and separation of fluorescent carbon nanoparticles from candle ashes. From the preliminary characterization of polychromatic fluorescent carbon nanoparticles (CNPs), we can see that carbon dots with different colors are obtained, and the particle size is less than 2 nm, the quantum yield is 0.8% ~ 1.9%. When the nanoparticles change from neutral solution to acidic or alkaline solution, the fluorescence intensity will be significantly reduced (40-89%).

1.4.3 hydrothermal method
Fluorescent CQDs were synthesized by mixing water with carbon source under high temperature and high pressure. Because of its simple operation, this method has been widely used in the preparation of CQDs. In 2014, Li [10] et al. Took anhydrous citric acid as carbon source, added chelating agent Mg (OH)₂ and passivator ethylenediamine (EDA), and then it was heated in the reactor for 3 hours at 200°C for 3 hours. After filtration and dialysis, water soluble polychromatic carbon dots with particle size of 0.8-2.8nm were obtained. The fluorescence quantum yield was 83%. Hydrothermal method was simple to operate and controllable, and it could be oxidized and modified in one-step reaction, which is conducive to mass production, And the reaction is carried out in a closed reactor, which can avoid the volatilization of toxic substances.

1.4.4 microwave synthesis
Zhu [11] et al. Used microwave method for the first time. They fully mixed carbohydrates and peg200 with water and dissolved them. They could quickly prepare dark brown carbon dots by microwave heating. PEG200 was used as both solvent and passivator, and the modification and reaction were completed in one step. When the reaction time was 5 min and 10 min, the particle size was (2.75 ± 45) nm, the fluorescence quantum yield was 6.3% and the particle size was (3.65±0.60) nm, and the fluorescence quantum yield was 3.1%. Fluorescent CNPs were prepared by microwave pyrolysis. This clean, cheap and convenient method shortens the reaction time and represents the potential progress of large-scale industrialization.

1.4.5 template method
In the process of CQDs formation, in order to control the growth of CQDs or avoid the agglomeration of carbon nanoparticles, the introduction of templates can effectively control the size of CQDs and prevent their agglomeration. Bourlinos [12] et al. Used template method to prepare carbon dots for the first time. They used NaY zeolite as template, and made 2,4-diaminophenol dihydrochloride react with zeolite surface by ion exchange. After heating and oxidation at 300°C, carbon dots formed on zeolite surface. After etching the zeolite template by hydrofluoric acid, carbon dots with fluorescence quantum yield of 0.1% and particle size of about 4 ~ 6nm were obtained.

1.5 Section overview
The above is a summary of the preparation of carbon quantum dots. It can be seen that from the discovery of carbon dots in 2004 to the first naming of carbon quantum dots in 2006, carbon quantum dots have been widely concerned, and more and more preparation methods have emerged. However, more efficient, simpler, greener preparation methods and improving the yield of fluorescence quantum
dots are also important goals of the follow-up research.

1.6 Chapter Summary
From an objective point of view, this article consults the literature to study the "top-down" and "bottom-up" preparation methods of carbon quantum dots, which are described in the first chapter. New discoveries are all described. Proceeding from reality, doing a lot of research is a necessary condition for scientific work. The objective expression of the discovery of carbon quantum dots is very important for the future and now.

2. Application of carbon quantum dots

| application          | author            | Materials used           | characteristic                  | literature                                                                 |
|----------------------|-------------------|--------------------------|---------------------------------|---------------------------------------------------------------------------|
| fluorescent probe    | Zhang[13] et al   | cucumber                 | Green, Specificity test         | Green synthesis of carbon nanoparticles and specific fluorescence detection of Fe^{3+} |
| Cell imaging         | Wang[14] et al    | Red carbon dots (RCD)    | Light stability, Fast response  | Red carbon dots as label-free two-photon fluorescent nanoprobes for imaging of formaldehyde in living cells and zebrafishes |
| Drug delivery        | Wenyu[15]         | Glucose-carbon quantum dots – cisplatin complex | Low toxicity and targeted effect on tumor | Preparation of glucose carbon quantum dots cisplatin complex and its anti breast cancer effect |
| LED device           | Wang[16] et al    | Sodium citrate and L-cysteine | Good fluorescence               | Promotion of micelle stability via a cyclic hydrophilic moiety |

Compared with semiconductor quantum dots and traditional organic dyes, carbon quantum dots not only have the advantages of low toxicity and good biocompatibility, but also have the characteristics of tunable luminescence, good fluorescence, photobleaching resistance, no flicker, easy functionalization, low cost and easy industrial production, so they have great development potential in many research fields.

2.1 Environmental detection - fluorescent probe
Luo[13] et al. Used fluorescence quenching method for selective detection of copper ion, it is proved that the mechanism is electrostatic quenching under electrostatic interaction. Fluorescence left-handed fluorescence was used to detect Cu^{2+} and curcumin in different types of environmental water samples and human serum samples, which provided a convenient strategy for the monitoring of Cu^{2+} and curcumin in environmental and biological samples.

2.1.1 Cell imaging
Wang[14] et al. Used red carbon dots for detection and imaging of intracellular formaldehyde. Red carbon point (RCD) is a two-photon fluorescence nanoprobe without labeling. It has good light stability, fast response speed (< 1 min), high sensitivity (~9.9 mmol/l) and selectivity to FA. Even under two-photon excitation, RCD can stain zebrafish tissues at intervals of 240 mm. Because of its compatibility and non toxicity, RCD is widely used in the biological imaging of bacteria and cells, which makes a great contribution to the understanding of intracellular formaldehyde related diseases.
2.1.2 Drug delivery
Wenyu\textsuperscript{[15]} synthesized carbon dots by microwave method, and then further became glucose targeted carbon dots cisplatin. Then, the physicochemical properties and biological cytology of the nanodrugs were characterized, and the antitumor effects of the nanodrugs were evaluated in vitro and in vivo respectively. The results showed that the glucose carbon quantum dots cisplatin complex was successfully prepared by physical and chemical characterization. Then, the biological cytological characterization showed that the carbon dots of nano carriers had low toxicity.

2.1.3 LED devices
Wang et al. \textsuperscript{[16]} synthesized green CDs with emission peak of about 500 nm by hydrothermal method using sodium citrate and L-cysteine as precursors. The mixture of green CDs and red phosphor is used as phosphor, and then combined with 395 nm UV chip to make white LED, which is suitable for indoor lighting.

2.2 Section overview
Not only the above, some of the prepared carbon quantum dots have excellent performance, but also are widely used in the fields of nano sensors, optical diagnostic agents and so on. There have been some achievements and progress in the application. The future application of the new type is still waiting for people to explore, and its practicability and environmental protection need to be improved in the application.

3. Preparation of carbon dots by ionic liquids

3.1 Biomass and ionic liquids
Among all kinds of carbon sources, biomass and its derivatives have attracted extensive attention because of their availability, low cost and renewable. Peanut shell, tea residue, bagasse, rice residue and other biomass were used as initial carbon sources to prepare CDs. As an important green solvent and functional liquid, ionic liquids have attracted much attention in recent years. For example, ionic liquids can destroy the chemical arrangement of cellulose in waste paper, and then make it dissolve rapidly under microwave radiation \textsuperscript{[17]}. Finally, the cellulose is recycled and further converted into fluorescence.

3.2 Application of carbon dots based on ionic liquids
Using 1-butyl-3-methylimidazolium chloride ([C4mim] Cl) and asparagine as carbon and nitrogen sources, Yang et al. Prepared nitrogen doped fluorescent carbon dots with quantum yield of 20.9% by one-step pyrolysis\textsuperscript{[18]}. The carbon point was dispersed in water, showing blue-green fluorescence, while the dry nitrogen doped carbon point powder showed yellow fluorescence under the ultraviolet light. It was used as a fluorescent probe for Hg\textsuperscript{2+} detection.

3.3 Section overview
The preparation and application of carbon quantum dots (CQDs) based on ionic liquids (ILs) is a new field. The extraction of green carbon sources from biomass, coupled with the special properties of ILs as modifiers, has attracted extensive attention of many people. At present, there are still great prospects in basic research and practical application.

4. Summary
As the latest carbon nano material, carbon quantum dots are not only more environmentally friendly, simpler to manufacture, and more versatile than previous metal quantum dots. This article summarizes some introductions of preparation and application on the basis of predecessors. It is not difficult to see that this is a very promising material, and there is a lot of potential waiting to be tapped, especially the hydrothermal method can increase research efforts, and its application is now extremely wide, in
environmental detection, biological imaging, etc. All are involved. In the next research, we want to extract carbon source from biomass and add ionic liquid as modifier to obtain a more environmentally friendly and more efficient preparation method. In short, as the advantages of carbon quantum dots are tapped, there is reason to believe that the future development prospects are very broad.

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