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Carbon Dots as Emerging Nanomaterials: A Sustainable Alternative to Quantum Dots

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Abstract

Carbon dots are a type of zero-dimensional nanomaterial, were first discovered in 2004 while cleaning single-walled carbon nanotubes using agarose gel and glass bead electrophoresis. Since then, carbon dots have become a main focus of research because they offer many benefits compared to traditional quantum dots. These benefits include cheaper production, eco-friendly ways to make them from natural sources, good water solubility, strong light stability, low harm to cells, and friendly interaction with living systems. Their surface can be easily modified, which makes them useful for many different applications. In recent years, carbon dots have shown a lot of promise, especially in creating sensitive gas sensors that can detect very small amounts of gas molecules, which are important for use in industries and healthcare. Also, carbon dots are useful for imaging inside the body and could help to solve environmental problems because of their selective fluorescence properties and surface chemistry. Their development represents a major move toward safer and more sustainable options than metal-based quantum dots.

Keywords: SWCNTs, cytotoxicity, biocompatibility, hydrophilicity, Gas sensors.

Introduction

Carbon dots are flexible 0D nanomaterials that were first developed in the early 21st century. They have numerous applications, including imaging, drug delivery, and disease diagnosis. They are safe for the body, less harmful, and inert, which makes them excellent candidates for use in antibacterial treatments. Carbon dots are usually small, round particles made of carbon with different types of bonds, like sp^2 or sp^3, and they may also have oxygen or nitrogen groups. These particles can be modified with other chemicals to form a structure that is either amorphous or crystalline. In this review, our content is divided into three main sections. The first part talks about how carbon dots are made, which includes two main methods: the top-down approach and the bottom-up approach [1]. The second part explains the optical properties of carbon dots, and the third part covers their main applications in comparison with quantum dots. We also discussed the current challenges and future possibilities for carbon dots. Carbon dots can be grouped into different categories depending on the structure of their carbon core, Carbon nanodots (CNDs).

1.1 Carbon Nanodots (CNDs)

It is a 0D, nearly spherical structure, amorphous that lacks proper quantum confinement but has a high level of carbon content [4]. Its size is under 10nm, rich in hydroxyl, carboxyl, and amino groups, which gives it special properties and makes it suitable for various applications like biomedicine, biosensing, and photocatalysis.

1.2 Carbon Quantum Dots (CQDs)

CQDs have size <10 nm. It has a crystalline/graphitic carbon core structure and exhibits quantum confinement [7]. The main functional groups attached are carboxyl, hydroxyl, epoxy and their fluorescence origin may be quantum confinement as well as surface states. They are mainly synthesized by electrochemical, hydrothermal and laser ablation methods.

1.3 Graphene Quantum Dots (GQDs)

It consists of π-conjugated 0D structure made up of single-layer or a few-layer graphene with a lateral size restricted to less than 20 nm. Their fluorescence origin can be quantum confinement and/or edge states.

1.4 Carbonized Polymer Dots (CPDs)

CPDs are a carbon/polymer hybrid 0D nanomaterial that consists of a carbon core surrounded by a framework of crosslinked polymer chains on its surface [8]. The main functional groups attached are residual polymer chains, amides, and hydroxyls.

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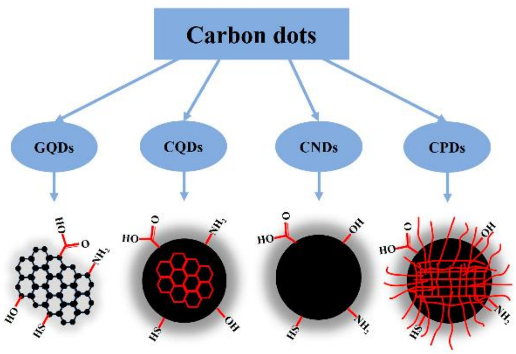

Fig.1. Classification of carbon dots. [18]

2. Synthesis of Carbon Dots

Almost any carbon containing material can be used to synthesizes CDs. Synthesis of CDs are broadly categorizing into two approaches: Top-down approach and bottom-up approach.

2.1. Top-Down Approach

In this method, larger carbon atoms are broken down into smaller nanoparticles using techniques like acid treatment, ultrasonic methods, hydrothermal or solvothermal exfoliation, and others. The process works by taking large-sized starting materials and subjecting them to various acid treatments to convert them into graphene-like carbon dots. This technique can also involve laser ablation, electrochemical oxidation, and chemical exfoliation. In the arc discharge process, when plasma is formed, an arc is created between an electrode made of carbon materials and a cathode. The carbon vapors generated in this process condense and cool down to form carbon dots. In laser ablation, a high-pulse laser is used to irradiate the target material, turning it into a plasma state. This plasma then crystallizes into carbon dots, which are dispersed in a suitable solvent to modify their surface [2-4]. A single or double pulse laser is used in laser ablation, with a second pulse in the double pulse method helping to create smaller carbon dots. One disadvantage of arc discharge is that it produces low yields, and it is used to make carbon dots with heteroatoms. Laser ablation, on the other hand, requires complex equipment for post-processing steps. In acid exfoliation, strong acids such as nitric acid or sulfuric acid are used to oxidize and break apart graphite, graphene oxide, coal, and other carbon materials. This process also introduces functional groups. In ultrasonic-assisted liquid-phase methods, ultrasonic waves help break down the carbon material into nanoparticles in acidic, alkaline, or oxidizing solutions. This approach is simple, time-efficient, and doesn't require extra treatments after the process. It is effective for producing carbon dots but has a low quantum yield. Hydrothermal exfoliation involves reacting carbon-based materials with organic salts dissolved in water inside a vacuum autoclave at high temperatures for several hours. This creates an intermediate compound, which is further broken down into graphene quantum dots and then purified and filtered.

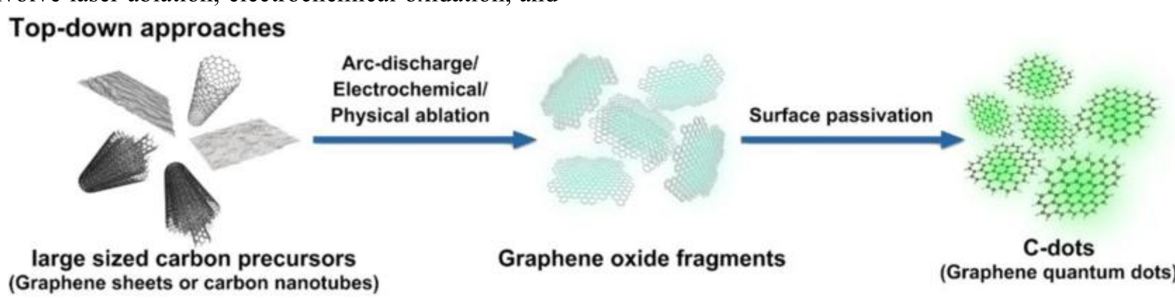

Fig.2. Schematic view of the top-down approach of CDs synthesis [17].

GQDs can also be made through an electrochemical process where carbon nanotubes are electrolyzed in a suitable electrolyte with proper counter and working electrodes, allowing control over surface functionalization [1]. Even though the top-down approach is cheaper and easier, it offers poor control over the size and uniformity of the resulting materials. Because of this lack of control, the specific surface area of the carbon dots decreases, limiting the number of active sites they can offer.

2.2. Bottom-Up Approach

In this method, carbon dots are made from smaller molecular precursors, which helps achieve better structural and chemical uniformity [2,5]. The mechanism of this technique is shown in Fig. 3, where smaller precursors undergo dehydration and then polymerization to form amorphous carbon dots. Some common bottom-up synthesis methods include hydrothermal treatment, solvothermal methods, pyrolysis, microwave pyrolysis, and irradiation. In hydrothermal treatment, a carbon precursor dissolved in water is converted into carbon dots in the presence of strong acids like HNO3, H2SO4, or H2O2 at high temperature and pressure. This involves dehydration followed by carbonization. The acids in the reaction mixture add hydrophilic surface groups such as carbonyls, hydroxyls, and carboxyls to the carbon dots [6,9]. The microwave-assisted reduction technique for carbon dot synthesis involves polymerization, dehydration, and carbonization. In this process, amine-rich precursors form cross-linked clusters that polymerize, then undergo intermolecular and intramolecular dehydration to create organic clusters with rich amine bonds. These clusters then carbonize to form carbon cores. The time and temperature of the carbonization step influence the optical properties of the produced carbon dots. Also, the duration of microwave treatment affects the size of the carbon dots, with 3-4 nm sized dots forming when treatment lasts 5-20 minutes [4,5]. This technique is widely used, energy efficient, and requires minimal equipment. In hydrothermal treatment, carbon precursors dissolved in water are converted to carbon dots in the presence of strong acids like HNO3, H_2SO_4, or H_2O_2 at high temperature and pressure, followed by dehydration and carbonization. These acids introduce hydrophilic surface groups such as carbonyls, hydroxyls, and carboxyls onto the carbon dots [3,10]. The advantage of this method is that it is eco-friendly, but it requires high reaction temperature and time. A wide range of precursors, such as citric acid, urea, polyamines, and biological sources like carbohydrates, amino acids, lignin, mushrooms, and polymers, are used for carbon dot synthesis through hydrothermal or microwave-assisted methods. In the solvothermal process, instead of water, various organic solvents like ethanol, glycol, and DMF are used to synthesize carbon dots. The choice of solvent affects the size and surface properties of the carbon dots, which can enhance their luminescence. Amphiphilic carbon dots, which are soluble in both polar and nonpolar solvents, can be produced using this technique. However, the downside of bottom-up synthesis is that these processes are complex and the resulting products often have poor solubility [4,13].

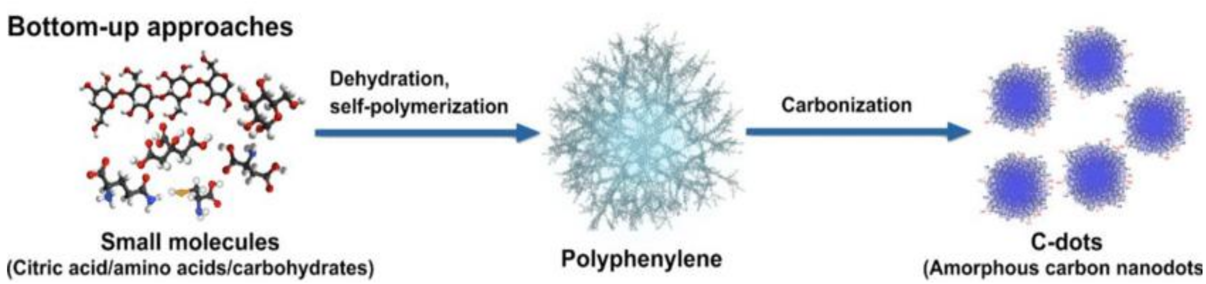

Fig.3. Schematic view of bottom-up approach of CDs synthesis [17].

2.3 Green Route Synthesis

Green synthesis typically uses a bottom-up method. When making carbon dots (CDs) through a green approach, the focus is on eco-friendly methods that reduce harmful by-products while still ensuring good quality and efficiency. This process often uses biomass like proteins, waste materials, and living organisms as starting materials, or it may use sustainable methods that work at room temperature. Carbon quantum dots (CQDs) can be made from things like orange juice, apple juice, carrot juice, rice bran, orange peel, and lemon peel. Table 1 shows how CQDs are made from various materials, along with the uses and features of the CQDs produced from each. Choosing the right material for making CDs is important because it affects how well the process works, the quantum yield, surface energy, electronic structure, and optical properties of the resulting CDs. Also, modifying the surface of CDs, known as functionalization, is crucial for their use in sensing. Certain groups like carbonyl (–C=O), carboxylic (–COOH), hydroxyl (–OH), and amine (–NH) on the surface of organic materials play a key role in the creation of CQDs. These groups also improve the fluorescent properties, water solubility, and functionalization of CQDs, and enhance surface activity, which leads to different ways they absorb light. These functional groups can be influenced by factors like reaction temperature. Many studies have focused on making CQDs from natural sources. For example, Wang and Hu reported that C-dots made from orange juice had a quantum yield of 26%. Similarly, the quantum yield from lemon and apple juices were 6.4% and 14. 86% to 24. 89%, respectively [4,13].

Green Route Synthesis			
Raw Material Used	**Synthesis Technique**	**Applications**	**Properties**
Lemon juice [13,14]	1.Microwave-assisted method 2.Hydrothermal Approach	Medical diagnostics Environmental monitoring Bioimaging	bright photoluminescence
Rice Bran [15]	1.carbonization and nano quantization 2.hydrothermal synthesis	Biocompatible	strong green fluorescence under UV light nontoxic.
Carrot Juice [12]	1.Enzymatic Treatment 2.Microwave Irradiation	Bioimaging and sensing	photoluminescence
Apple juice [11,12,13]	Hydrothermal treatment at 190°C for 12 hours	Biomedical Applications: drug delivery, cancer theragnostic etc.	pH-dependent fluorescence

Table 1. Green route synthesis: synthesis technique, applications and properties

3. Optical Properties

Doping agents and solvents help improve the optical properties of carbon dots. They increase the quantum yield, cause a redshift in the emission spectrum, and boost the production of reactive oxygen species, which are important for photodynamic therapy. Carbon dots show several types of luminescence, including photoluminescence, chemiluminescence, electrochemiluminescence, fluorescence, up-conversion photoluminescence, and phosphorescence. The emission from carbon dots changes with the excitation wavelength, and as the excitation wavelength increases, the emission becomes redder. Amphiphilic carbon dots show solvatochromism, where their absorption and emission spectra depend strongly on the polarity of the solvent [6].

3.1. Photoluminescence (PL)

Photoluminescence is divided into fluorescence and phosphorescence. This happens when an electron moves from the lowest unoccupied molecular orbital to a higher occupied molecular orbital. The luminescence of carbon dots can be modified by controlling condensation reactions, chemical changes, or by doping with elements like nitrogen, boron, sulfur, and phosphorus [6, 9-11]. Among these, nitrogen is commonly used. The photoluminescence properties of carbon dots change with their size. Small dots emit in the ultraviolet range, medium-sized ones in the visible range, and larger ones in the infrared range. A red shift in emission occurs when the band gap narrows due to changes in functional groups.

3.2 Fluorescence (FL)

Carbon dots emit fluorescence across a wide range from ultraviolet to near-infrared. The main reasons for fluorescence include core state emissions, surface state emissions, and molecular fluorescence. Due to quantum confinement, the fluorescence emission shifts to longer wavelengths as the size of the carbon dots increases. Doping with sulfur, phosphorus, and nitrogen can enhance the quantum yield through surface passivation [6-8, 11]. When the doped atom has high electronegativity, the emission wavelength becomes shorter, and the quantum yield increases. Controlling the concentration of the dopant can adjust fluorescence emission. Carbon dots have a very short fluorescence lifetime, typically in nanoseconds, and it's challenging to make them with longer lifetimes. However, recent advancements have enabled the creation of carbon dots with orange and red emissions for use in optical-electronic sensors. Red and orange shifts are due to larger particle sizes and higher nitrogen content.

3.3 Phosphorescence (P)

Phosphorescence at room temperature involves electrons changing their spin state as they move from a triple-exciton state to the ground state, which takes a long time. This results in stronger visual signals.

3.4 Chemiluminescence (CL)

Chemiluminescence is luminescence caused by chemical reactions. It's believed that energy differences in the surface states of carbon dots lead to chemiluminescence. Research indicates that chemiluminescence occurs when carbon dots interact with strong oxidants that oxidize their orbitals. It also happens due to electron-hole annihilation and the radiative recombination of electrons and holes injected into the carbon dots.

4 Advantages of Carbon Dots over Quantum Dots

Carbon dots offer several advantages over traditional quantum dots, especially in biocompatibility, toxicity, and synthesis methods. These qualities make them appealing for a variety of applications, particularly in biomedical fields.

4.1 Biocompatibility and Toxicity

Carbon dots are biocompatible and have low toxicity, which makes them safer for biological applications compared to quantum dots that often contain toxic heavy metals. Their non-toxic nature allows broader use in medical imaging and drug delivery systems without the risks associated with quantum dots [8].

4.2 Synthesis and Functionalization

Synthesizing carbon dots can be done through eco-friendly methods such as hydrothermal carbonization and microwave synthesis, which are simpler and less expensive than the complex processes needed for quantum dots. Carbon dots can be easily modified on their surfaces, making them versatile for targeted drug delivery and biosensing [10,15].

4.3 Optical Properties

Carbon dots can be tailored for specific fluorescence emissions by adjusting the excitation wavelength. They are also resistant to photobleaching, ensuring stability in imaging applications [7,9].

Conclusion

Carbon dots have promising applications in various fields, especially sensing and biomedicine. They are a promising new carbon nanomaterial with unique physical and chemical properties. Their low toxicity, good biocompatibility, and ease of surface modification make them suitable for biological environments where safety is crucial. Carbon dots show potential for use in bioimaging, targeted drug delivery, disease diagnosis, and therapy. Their optical and electrical properties can be controlled by adjusting the degree of carbonization and functionalization during synthesis. Currently, research is exploring multi-gas sensing films and multi-array gas sensors based on carbon dots, which are popular topics in scientific research. Despite these advantages, carbon dots made from natural precursors often have low quantum yield and chemical inhomogeneity. Their response to pH and temperature also needs to be better optimized. More efforts are needed to develop highly sensitive, selective, and stable gas sensors that work at room temperature. Therefore, carbon dots have high potential as gas sensors due to their large surface area, conductivity, and other essential properties that make them effective materials for sensing.

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