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Photoluminescent carbon nanodots for artificial photosynthesis

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Abstract

The emerging field of carbon dots (CDs), a type of carbon nanostructure that has gained significant attention due to its unique properties and potential applications. CDs possess remarkable attributes, including photoluminescence, electrochemical potential, compatibility with living organisms, solubility in water, chemical stability, and versatile surface properties. The chemical structure, particle size, and surface functionalities of CDs all have an impact on their photoluminescent properties, which are the focus of this review. The photoluminescence mechanism in CDs is discussed, highlighting their amorphous structure, and comparing them to graphene quantum dots. The paper delves into the application of CDs in artificial photosynthesis, which enhances crop growth by improving the photosynthesis process. CDs increase sunlight and carbon dioxide absorption rates by interacting with plant leaves, potentially leading to substantial crop yield improvements. The advantages of CDs in artificial photosynthesis are explored, including their modifiable absorption characteristics across the ultraviolet to near-infrared spectrum. The paper acknowledges challenges in CD production, such as size control and aggregation, while emphasizing their potential in various fields, including sensing, bioimaging, energy devices, and catalysis. CDs' unique optical properties and versatile applications suggest a promising future for these nanostructures in numerous scientific and technological domains.

1. Introduction

Carbon dots (CDs) have captured the scientific community's interest in the relatively new realm of carbon nanostructures [1-6]. Their unique attributes, such as photoluminescence, electrochemical potential, compatibility with living organisms, minimal harm, excellent dissolubility in water, chemical endurance, and adaptable surface properties, have sparked great enthusiasm for their potential uses in diverse fields like light-based electronics [7], storing energy [8], stimulating chemical reactions [9], detecting substances [10], and medical applications [11,12].

Derived from carbon-rich sources like organic and polymeric materials, CDs exhibit excellent physiochemical properties. Particle sizes for CDs are typically below 10 nm and consist mainly of carbon, hydrogen, and oxygen. Multiple synthetic strategies create CDs [13]. Recent investigations have unveiled how CDs amplify plants' efficiency and improve agriculture yield [14,15]. CDs can enhance agronomic parameters and increase yields in plants or crops by activating different biological processes, including photosynthesis. Furthermore, they have shown potential as sensing platforms for postharvest applications, effectively analyzing agricultural products and ensuring food safety quality [16].

This review highlights the potential of CDs as energy conversion materials for artificial photosynthesis applications. Photoluminescence occurs when a substance absorbs light photons and subsequently emits those photons at lower energy levels. When subjected to light, substances like CDs take in the energy from photons, elevating their electrons to higher energy states. Photoluminescence is crucial in mimicking the natural photosynthesis process of plants. It captures and converts light into energy, releasing excess energy as emitted light when the electrons return to their original states. Researchers are investigating the potential of utilizing CDs' photoluminescence abilities to create renewable energy sources [17]. These efficient light harvesters may drive chemical reactions like plants that convert carbon dioxide into glucose during photosynthesis [18].

2. Properties and synthesis

CDs possess tunable optical characteristics like fluorescence, photoluminescence, and chemiluminescence, making them highly promising for developing optical devices. This review focuses on photoluminescence, a property closely related to the chemical structure, particle size, and surface functionalities of CDs. CDs primarily consist of hydrocarbons and oxygen, resulting in hydroxyl, carbonyl, and carboxyl functional groups and sp^2 C=C and C=O bonds, as depicted in Figure 1, collectively defining CDs' chemical structure and surface functionalities [19].

The high surface area of CDs allows for efficient interaction with other molecules, enabling enhanced sensing capabilities and potential applications in catalysis and energy storage [20]. The tunable emission wavelength of CDs makes them versatile in different imaging and sensing applications, where specific emission wavelengths are desired for optimal performance [21]. Furthermore, CDs' biocompatibility and low toxicity are critical for their use in biomedical applications such as bioimaging [22] and drug delivery [5]. These properties ensure minimal adverse effects on living organisms and enhance the safety and efficacy of CD-based biomedical products.

CDs are produced using various synthetic techniques involving three main steps: carbonization, passivation, and surface functionalization [23,24]. In recent years, carbonization through pyrolysis has emerged as a potent technique for producing fluorescent CDs, utilizing macroscopic carbon structures as precursors. This method boasts several advantages, including rapid reaction times, cost-effectiveness, ease of operation, solvent-free processes, and scalability. The pivotal processes of heating, dehydration, degradation, and carbonization play crucial roles in converting organic carbon-containing substances into CDS under high temperatures. During pyrolysis, carbon precursors undergo cleavage into carbon nanoparticles, typically facilitated by high-concentration alkali or acid. This intricate process of carbonization involves the conversion of carbon-containing precursors into carbon nanomaterials. It's imperative to note the sensitivity of this process, necessitating precise temperature control due to its endothermic nature. Extreme temperature fluctuations can lead to incomplete carbonization or over-oxidation, resulting in the degradation of CDs. Hence, meticulous temperature regulation is indispensable for ensuring the quality and integrity of the final product. [25-27].

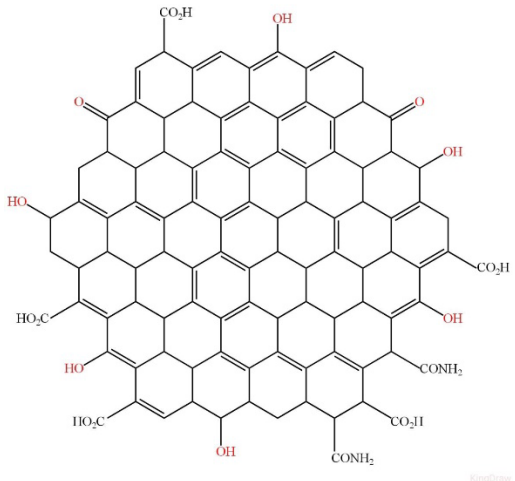

Figure 1. Carbon Dots Chemical Structure.

However, carbonization via hydrothermal reaction in the presence of sucrose entails the hydrolysis of sucrose to produce fructose and glucose. When generating CDs from biomass components such as cellulose, hemicellulose, chitin, or lignin, cellulose degradation during the hydrothermal process occurs at temperatures surpassing 200°C. Initially, the physical structure of cellulose disintegrates via hydrolysis, converting long-chain cellulose into oligomeric compounds comprising carbon, hydrogen, and oxygen elements, which subsequently transform into glucose. These smaller compounds undergo isomerization, dehydration, and decomposition, resulting in soluble intermediates like furfurals, organic acids, ketones, and aldehydes. Hydronium ions, formed from these acids, then serve as catalysts, aiding in the dehydration, polymerization, condensation, and conversion of these intermediates into soluble polymeric products. Aromatization reactions and the formation of aromatic clusters occur through aldol condensation and cycloaddition reactions. CDs form through a single burst nucleation once the concentration of these aromatic clusters surpasses a critical supersaturation point. Furthermore, residual precursors like hydrophilic and oxygen-containing fragments present in the solution tend to linger around the surface of the cluster, forming a passive layer and resulting in CDs with a hydrophobic core and a shell abundant in functional groups [28-33].

Passivation improves emission properties by reducing surface defects and reaction sites. This step, which involves the covalent bonding of amine-containing agents, is a common method employed to enhance the fluorescence properties of CDs [34]. It also provides stability and increasing shelf life due to the increased optoelectric property that forms a thin insulating capping layer that will shield the CDs from impurities and further improve fluorescence intensity [35-37].

The last crucial step is surface functionalization, which enables the production of task-specific CDs. This process will tune the functional groups on the surface of CDs to create or change the surface states that will guide and expand their application range [38]. Surface functional groups have a profound impact on the characteristics of CDs. Among the most common groups encountered in CDs are amino, carboxy, and hydroxy. These groups can be incorporated through both covalent methods—such as amide coupling reactions, silylation, and other techniques like esterification, sulfonylation, and copolymerization—as well as noncovalent approaches, including π interactions, complexation/ chelation, and electrostatic interactions [39].

Over time, numerous synthetic approaches have been developed for making CDs, broadly categorized as top-down and bottom-up methods depicted in Figure 2 [9].

The conventional methods involve the pyrolysis of organic precursors like citric acid, glucose, chitosan, fruit juice, and rice. However, organic waste materials such as banana peels, citrus peels, vegetable waste, rice husk, wheat straw, pencil battery electrodes, wastepaper, and plastic can also be transformed into CDs [40,41].

Synthetic methods play a vital role in achieving CDs with precise control over their morphology, size distribution, surface functionality, and tunability. These properties can be further adjusted through surface modification or choosing different synthetic routes, resulting in CDs with various desirable characteristics according to the studies conducted [42,43]. The subsequent section will delve into the types of synthetic methods of CDs.

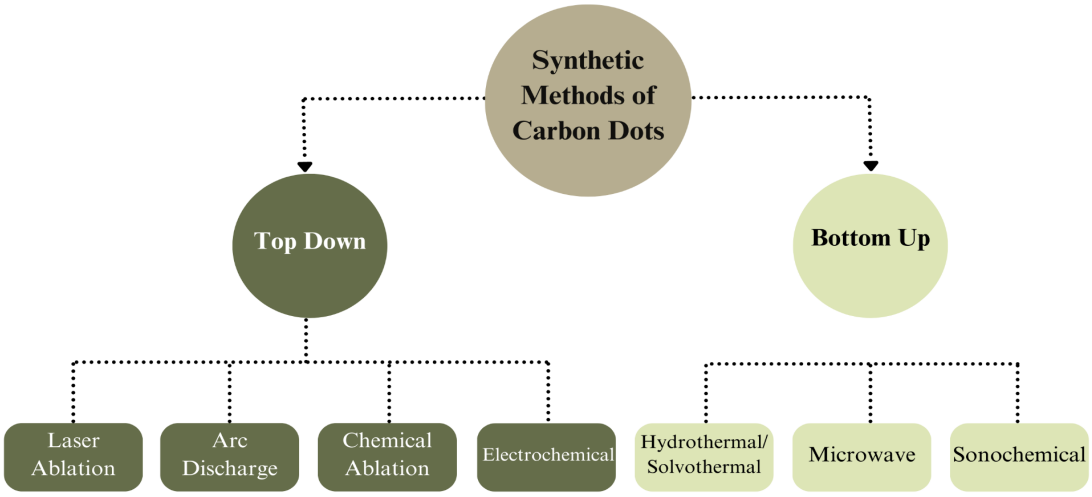

Figure 2. Methods for synthesizing carbon dots.

2.1 Bottom-up method

This approach involves the synthesis of CDs from small molecules using chemical reactions such as polymerization or carbonization. Several techniques have been employed, including hydrothermal or solvothermal methods, pyrolysis, sonochemical processes, and microwave irradiation [44].

2.1.1 Hydrothermal/Solvothermal treatment

Hydrothermal or solvothermal synthesis represents a straightforward, fast, and economical approach for producing hydrophilic soluble CDs. In this method, a carbon-containing precursor is combined with a solvent and enclosed within a sealed autoclave. The mixture is then subjected to high temperatures ranging from 100°C to 300°C for a specific duration, generating elevated temperatures and pressure within the autoclave. Figure 3 illustrates a schematic diagram depicting the hydrothermal/solvothermal treatment process. These conditions facilitate the breakdown of carbon molecules, resulting in the formation of CDs. Gogoi and Khan (2018), in their study, produced CDs using a precursor of starch and citric acid. The process involved dissolving citric acid in deionized (DI) water, which was then placed in an autoclave and heated to 150°C for 5 h. Afterward, centrifugation and dialysis were employed to eliminate unreacted or large-sized particles, thus purifying the CDs. Transmission electron microscopy (TEM) analysis revealed that the CDs exhibited an average diameter below 5.0 nm, ranging from 3.0 nm to 3.2 nm, with a layer spacing of 0.37 nm [45]. In another study, Nammahachak *et al*., 2022 achieved hydrothermal carbon quantum dots (CQDs) with sizes ranging from 4 nm to 15 nm by varying the filling volumes of sucrose solution in the hydrothermal reactor. The sucrose concentration, hydrothermal autoclave, and temperature profile were kept constant during the synthesis. The differences in CQD sizes were primarily influenced by the filling volumes, indicating the significance of the heterogeneous surface between the precursor and reactor. Thus, in addition to considering traditional experimental parameters like precursor concentrations, processing temperatures, and reaction times, the heterogeneous interfaces also played a crucial role in determining the CQD sizes [46].

2.1.2 Microwave-assisted synthesis

Milosavljevic *et al.* (2014), utilized a microwave-assisted method to synthesize carbon quantum dots from citric acid and ascorbic acid as precursors [47]. They incorporated polyethylene glycol (PEG), polyvinylpyrrolidone, and bovine serum albumin as capping agents during the synthesis. The process involved mixing the acid solution with the capping agent and subjecting it to microwave radiation at 300 W power for 20 min, from 60°C to 140°C. The researchers noted that synthesizing the CDs at temperatures below 120°C was challenging, while the range of 120°C to 140°C was more suitable for producing small CDs with blue fluorescent properties [47]. According to the study of Nawarat, they used a simple and eco-friendly microwave-assisted method to prepare carbon dots, similar to those obtained from fruit peels [48]. The carbon dots produced were slightly larger in diameter and atomic lattice space but still comparable in properties using 800 W for 2 min. The UV-vis and FTIR results showed similar electronic structures with minor differences from other carbon dots. The carbon dots from rambutan peels exhibited better fluorescent properties in imaging than DI water. Although not yet ready for practical bioimaging applications, the carbon dots have the potential for further research [48]. The schematic diagram of the microwave-assisted synthesis procedure is presented in Figure 4.

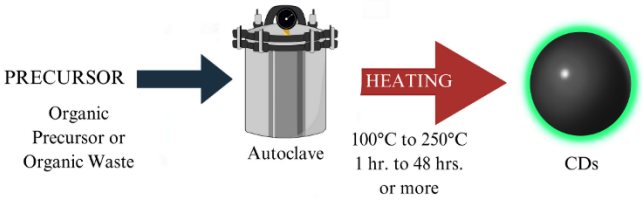

Figure 3. Schematic illustration of Solvothermal/Hydrothermal Treatment.

Figure 4. Schematic illustration of Microwave-Assisted Synthesis.

2.1.3 Sonochemical

Kumar *et al.* (2016) employed a sonochemical technique to synthesize CDs using polyethylene glycol (PEG) as the carbon source material [49]. In this process, the PEG solution underwent sonochemical treatment at various temperature ranges from 4°C to 150°C, with different time intervals ranging from 0.5 h to 3 h as shown in Figure 5. The optimal conditions for achieving the most favorable CD synthesis were a temperature of 75°C, a sonication time of 2.5 h, and an amplitude of 70%. The resultant CDs exhibited a quantum yield (QY) of approximately 16.0% and an average particle diameter of 27 nm [49].

Similarly, the same researchers utilized the sonochemical method to produce CDs from the PEG precursor, introduced by PEG into a quartz test tube. They heated it to 75°C, then subjected it to ultrasonic irradiation with a high amplitude for 2.5 h. They also employed this approach to generate hybrid nanocomposites known as tin-functionalized CDs (Sn@CDs) by incorporating Sn metal into the PEG solvent. High-resolution transmission electron microscopy (HRTEM) analysis revealed that the average sizes of the CDs and Sn@CDs were 5 nm and 7 nm, respectively.

2.2 Top-down method

This approach produces small carbon dots (CDs) from large molecules through pyrolysis or decomposition using various chemical or physical techniques, including arc discharge, laser, chemical, and electrochemical oxidation methods [50].

2.2.1 Laser ablation

Laser ablation serves as a technique to produce a range of nanomaterials, such as CDs, carbon nanotubes, nanowires, and core shell nanomaterials. This process involves the formation of nanomaterials through the nucleation and growth of laser-vaporized substances within a surrounding gas environment. The particles resulting from ablation, comprising ions, atoms, and atom clusters, are heated by the laser beam to temperatures of up to several kilokelvins. Subsequently, they interact with the surrounding liquid, leading to chemical reactions within the cavitation bubble. During the plasma cooling phase, nanoparticles are formed, diffusing into the surrounding liquid to create a colloidal solution. This entire cycle takes approximately 1 ms. The rapid quenching of the vapor offers a distinct advantage in yielding nanoparticles of exceptional purity within the quantum size range (< 10 nm) [51]. Nanomaterial synthesis via laser ablation relies on precise control of numerous variables, such as laser intensity, process temperature, geometric factors, carrier gas composition, gas pressure, and flow dynamics [52].

This technique directs a highly energetic laser beam at the precursor molecule, leading to elevated pressure and temperature. The rapid heating causes the target molecule to evaporate and form plasma, which subsequently condenses to produce CDs with a uniformly small size [53] as shown in Figure 6. Kaczmarek *et al.* prepared CDs from graphite in a polyethyleneimine and ethylenediamine solvent mixture. They exposed a laser beam with a wavelength of 532 nm and a pulse time of 10 ns to a graphite electrode for 15.0 min, using a laser fluence of 3.5 J·cm^{-2}. The resulting suspended particles were dialyzed and purified to obtain pure CDs with a size ranging from 1.0 nm to 3.0 nm [54]. On the other hand, Thongpool *et al.* utilized laser ablation to produce carbon dots (CDs). This process involved applying 5000 pulses on graphite, resulting in the formation of a suspension containing CDs. Subsequently, the suspension underwent an additional laser irradiation of 25,000 pulses with continuous stirring, which also facilitated the removal of larger particles to yield CDs. [55].

2.2.2 Arc discharge

The arc discharge technique creates small quantum dot (QD) molecules from initial bulk materials. This method involves subjecting the bulk materials to a high-temperature gas plasma within a sealed container. The intense heat, generated through electric current, transforms the carbon precursor into vapor form, leading to its condensation and the production of small CDs [53]. For example, Chao-Mujica *et al.*, synthesized CDs using graphite electrodes in a water-based solution. Here, graphite functioned as both the cathode and anode. [56] Submerging the electrodes in water, they applied a solid current to exfoliate the anode fully, as depicted in Figure 7. The resulting materials, mainly carbon nano onions, were separated from the solution. Afterward, these materials were allowed to settle for several hours, facilitating the removal of larger particles containing carbon nanotubes. The soluble fraction mainly comprised CDs, separated through decantation to yield high-purity CDs. Characterization analysis revealed that the particle sizes ranged from 1.0 nm to 5.0 nm, exhibiting notable fluorescent properties [38]

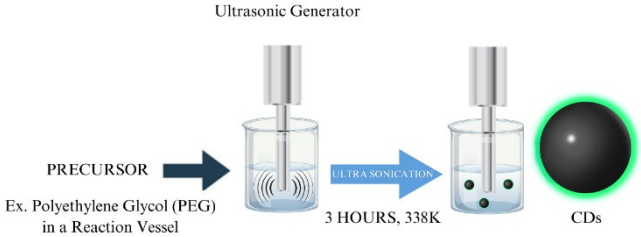

Figure 5. Schematic illustration of Sonochemical.

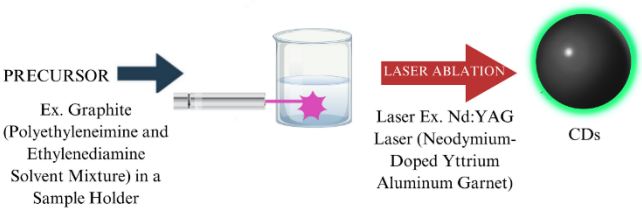

Figure 6. Schematic illustration of Laser Ablation.

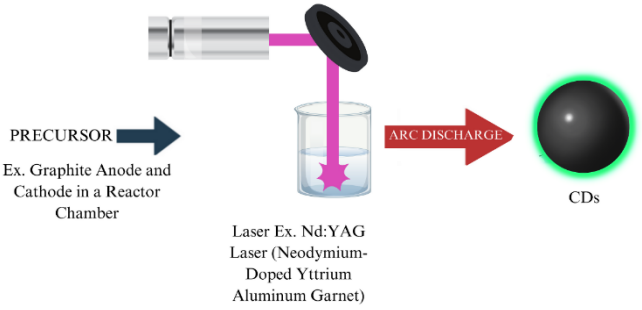

Figure 7. Schematic illustration of Arc Discharge.

2.2.3 Chemical ablation

Chemical ablation entails the conversion of carbonaceous nanomaterials through the application of a potent oxidizing agent to organic molecules. Furthermore, controlled oxidation can fragment these nanomaterials into smaller sheets. However, the efficacy of this process is contingent upon variables such as acid concentration and treatment duration, potentially affecting the precise synthesis of CDs. Figure 8 depicts the schematic diagram of the chemical ablation method [57].

Feng *et al.*, generated blue fluorescent CDs from Coke with a quantum yield (QY) 9.2. These CDs were employed in the creation of a light-emitting diode. Their procedure treated coke powder in a mixture of H_2O_2 and H_2O (20 mL:30 mL) under ultrasonication. To obtain pure CDs, the solution was subsequently continuously heated, filtered, and dialyzed [40]

Similarly, Tan *et al*. developed CDs from a precursor of activated carbon sourced from coconut shells. This was achieved through the potent oxidizing agents HNO_3 and $HClO_4$ [59]. The carbon precursor was mixed with the acidic solution and exposed to microwave radiation at 100°C for 2 h. After cooling and neutralizing to pH 7.0, the solution was purified through several steps. The researchers highlighted that the resulting CDs exhibited minimal cytotoxicity, exceptional photostability, and biocompatibility and held the potential for bioimaging applications.

2.2.4 Electrochemical oxidation

This technique is potent for creating CDs from abundant carbon materials. Within this method, electrodes like graphitic rods, pencil rod extracts from batteries, and others are submerged in an electrolyte solution of either an acidic or essential nature [58]. A predetermined potential difference is then applied between these electrodes to induce the exfoliation of the electrode material, leading to the production of CDs, as shown in Figure 9. These CDs are subsequently isolated, separated, and purified to yield high-purity CDs.

Ming *et al*. (2012), employed electrochemical exfoliation to synthesize CDs from a graphitic electrode [60]. They immersed the graphitic rod as an electrode in Mili Q water with a separation distance of 7.5 cm. A direct current (DC) of 15 V to 60 V was supplied to the electrode for 2 h. The resulting solution exhibited a dark-yellow hue and was then subjected to washing and purification processes to obtain hydrophilic, water-soluble CDs in their pure form.

Likewise, Devi *et al*. (2017), generated CDs from a graphitic rod, yielding particles of approximately 7.0 nm in size [61]. In their electrochemical exfoliation method, they ran a direct current (DC) of 50.0 mA through a graphite rod that was submerged for 2 h in a basic electrolyte solution made of NaOH and EtOH. Their mechanistic investigation revealed that free OH- ions reacted with the anodic graphitic electrode, inducing a layer-by-layer exfoliation process that resulted in the formation of CDs. They observed that neither an aqueous solution devoid of EtOH nor EtOH without NaOH could produce CDs, thus highlighting the crucial role of NaOH in generating the necessary free OH^- ions for effective graphitic anode exfoliation.

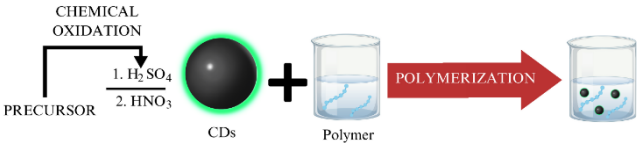

Figure 8. Schematic illustration of Chemical Ablation Method.

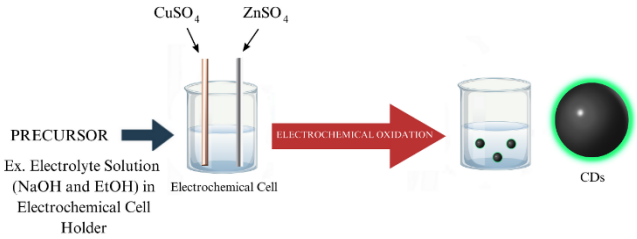

Figure 9. Schematic illustration of Electrochemical Oxidation.

3. Mechanism of photoluminescence

CDs are created using various methods and carbon-based starting materials. They display impressive traits like strong absorption, photoluminescence, fluorescence, phosphorescence, and chemiluminescence. CDs possess abundant oxygen-related features and come with an electronic bandgap. Multiple factors, such as particle size variations, surface imperfections, trapping sites, and surface structure, play a significant role in shaping the distinct optical characteristics of CDs. CDs are primarily characterized by their amorphous structure and share some similarities with graphene quantum dots regarding specific properties. However, there are noticeable distinctions in their surface functionality and crystalline composition. These differences are evident in how they exhibit electronic transitions and incorporate vibrational and rotational transitions. Multiple transitions in CDs contribute to their significant absorption in the UV-Vis region [62].

3.1 Photoluminescence characteristics and electronic transitions

Electronic transitions are evident in CDs, encompassing vibrational and rotational transitions. The numerous transitions lead to strong absorption within the UV-Vis region, occasionally manifesting robust emissions in the near-infrared region. The multiemission luminescence mechanism observed in CDs, characterized by various emission peaks, can be attributed to the presence of diverse emitting centers within the CDs. These emitting centers may originate from various sources such as different surface functional groups, quantum confinement effects, or defect states within the carbon structure [62], as illustrated in Figure 10.

Optical absorption within the UV range (200 nm to 400 nm) exhibits weak absorption within the visible range (380 nm to 750 nm). The electromagnetic spectrum indicating the visible light spectrum is shown in Figure 11. Notably, CDs' functional groups and electronic transitions, like π-π* and n-π*, influence absorption peaks. Specifically, π-π* transitions in sp^2 (C=C) bonds lead to absorption peaks around 240 nm,

while n-π* transitions in C-O bonds result in peaks around 340 nm. Figure 12 illustrates the functional group associated with each electronic transition in UV-visible spectroscopy. Surface treatments, modifications, and heteroatom doping can shift absorption peaks; for instance, amine and carbonyl functionalities induce redshifts in UV-Vis spectra [64].

Regarding CDs, exceptional properties were observed by Nie *et al.* (2014). Two types of CDs were prepared, exhibiting excitation-independent blue and excitation-dependent full-color emissions. The introduction of C-O and C-N functional groups created new energy levels, enabling full-color emission, and potentially useful for pH sensors [63].

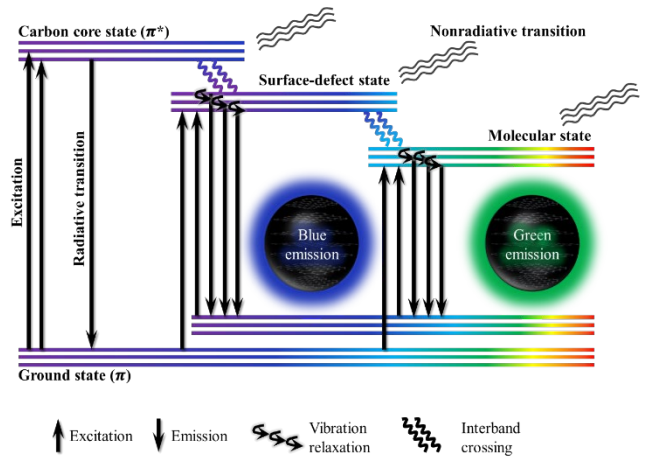

Figure 10. Multi-emission Luminescence Mechanism of CDs.

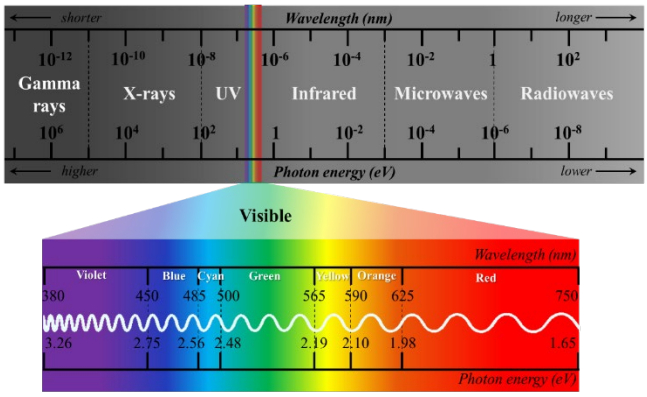

Figure 11. Electromagnetic Spectrum.

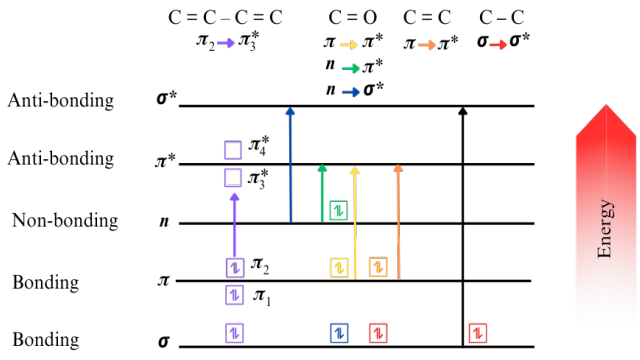

Figure 12. UV-Visible Spectroscopy electronic transition.

CDs showcase intriguing photoluminescence behavior wherein excitation wavelength influences emission peak and intensity [64]. Typically, photoluminescence peaks are seen in the blue and green regions, although single CDs can emit various photoluminescence spectra. This behavior can be altered through different synthesis routes, precursors, and surface treatments. Photoluminescence intensity quantitatively determines the quantum yield (QY), influenced by synthetic methods and post-treatment. CDs synthesized bottom-up tend to exhibit higher QY than top-down methods [5,66]. According to the study conducted by Ding *et al.*, the luminescence of CDs can vary from blue to red under a single wavelength of UV light, with a similar distribution of particle size and graphite structure in their carbon core. This variation occurs as the degree of surface oxidation increases, leading to a reduction in the band gaps [67]. On the other hand, Kandasamy ascribes that the alteration in the emitted color of CDs stems from the presence of dopant elements/heteroatoms, including boron (B), fluorine (F), nitrogen (N), sulfur (S), and phosphorus (P) [68].

Fluorescent carbon dots (CDs) display modifiable absorption traits within the ultraviolet (UV) range, extending into a prolonged tail that spans the visible near-infrared (NIR) region, it exhibits notable light absorption properties that can accept and donate electrons. Consequently, researchers focused properties of CDs in their light-harvesting capability. The interaction between the UV absorption profile and the electronic transitions occurring in the CDs' central core and the surrounding shell is visually represented in Figure 13. In this illustration, the body (depicted in blue) pertains to the encasing functional groups.

The spectral bands emerging below 300 nm (Band I in Figure 13) correspond to the π-π* transition linked to aromatic C=C bonds. Additionally, the Band ranging from 300 nm to 400 nm (designated as Band II in Figure 13) aligns with the n-π* transition originating from the C_5O bond within the carbon cores. As we move beyond 400 nm wavelengths (illustrated as Bands III to V in Figure 13), the observable bands signify transitions associated with surface states featuring unpaired electrons.

Notably, the n-π* transition and the broader surface state absorption bands typically overlap rather than being distinct or isolated. This overlapping nature leads to minimal divergence within the emission spectrum. A smooth color shift becomes apparent as the excitation wavelength varies.

It is worth mentioning that the lower-energy absorption band around 300 nm arises from charge transfer transitions involving n-π* and π-π* interactions, possibly including interlayer charge transfer that integrates a significant π-π* component. Although structural or energetic disorder, environmental conditions, deprotonation, and excitonic coupling influence the spectra, they do not significantly alter the overall pattern.

The phenomenon of red-shifting within the UV-Vis absorption spectrum, spanning from 420 nm (Band III in Figure 13) into the NIR spectral region (Band V in Figure 13), is attributed to incorporating graphitic nitrogen into the sp^2 carbon lattice. These graphitic nitrogen centers introduce additional electrons into unoccupied π* orbitals, resulting in a noticeable reduction in the HOMO to LUMO gap and a subsequent decrease in the energies associated with corresponding optical transitions.

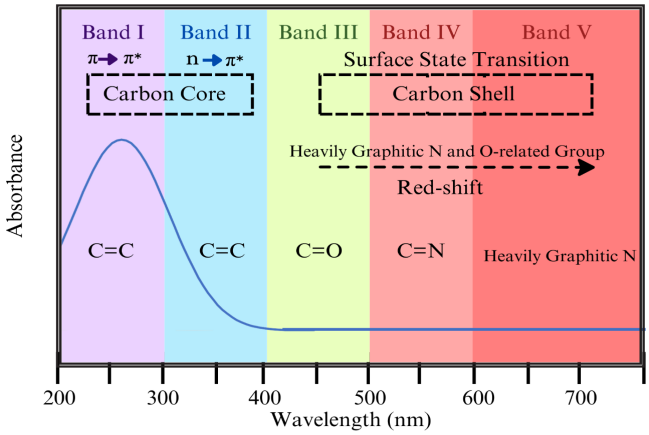

Figure 13. Variation of Absorption Spectra and Electronic Transitions of Carbon Dots

Simultaneously, oxygen-containing functional groups like hydroxyl, carboxyl, and epoxy, present on the surface, can also impact energy levels, culminating in a red-shifted absorption phenomenon, as discussed by Liu, 2020 [5]. As previously discussed, carbon dots (CDs) possess notable light absorption capabilities and distinctive electron acceptor/donor properties. This characteristic has spurred extensive research into their potential for efficient light harvesting. The absorption capacity of CDs mainly originates from their sp^2 hybridized graphitic core and surface functional groups. UV-visible spectra of CDs showcase two prominent absorption peaks, approximately around 240 nm and 350 nm. The first peak arises from π to π* transition within the sp^2 graphitic domain, while the second peak is attributed to the n-π* change involving C_5O-containing groups. In some instances, a supplementary shoulder peak near 450 nm can be observed due to the presence of COOH groups [69]

Despite all the significant advancements in understanding the photoluminescence (PL) mechanism of CDs, the detailed and exact mechanism remains a subject of exploration due to the complexity of the structures and surface functionalities. Different factors may add especially the surface state, carbon core state, and molecular state have been proposed to expound the PL mechanism [70-73]. To understand the PL mechanism, researchers have explored the relationship between CDs' surface chemical bonds and their optical properties. UV-Vis absorption spectra and Fourier transform infrared (FT-IR) were used to study the CDs in their protonation degrees of the carbon source. Changes in the transitions are a guide where the surface chemical bonds occur in the PL mechanism of CDs.

3.2 Surface functional group

In our study, the utilization of Fourier-transform infrared spectroscopy (FTIR) analysis confirmed the existence of bond stretching involving -SH, $-SO_2$, $-NH_2$, and CON-H groups after the incorporation of L-cysteine. This observation indicates potential S, N-doping of the carbon dots, which is responsible for the alterations in photoluminescence properties [74].

The optical characteristics of CDs are intricately linked to their structure. Although the specific structural features of CDs are currently under investigation, it is known that CDs have a pseudo-spherical shape with a graphitic core composed of a sp^2 hybridized carbon network. The outer layer contains surface functional groups, and the interlayer spacing in CDs is higher than the graphitic spacing (0.33 nm), mainly due to the presence of oxygen functional groups. The nature of these surface functional groups depends on the starting materials used. Commonly used carbohydrate-derived CDs primarily contain oxygen functional groups, with a predominance of the -COOH group. These surface groups play a crucial role in influencing CDs' surface energy and energy gap of CDs, and surface passivation enhances their optical properties.

The extent of oxidation of surface groups can significantly impact the optical properties of CDs. Most CDs are synthesized using oxidative strategies, producing a high oxidative state. However, reducing the surface groups has enhanced fluorescence properties, including increased quantum yield, fluorescence intensity, and fluorescence lifetime. Moreover, the degree of oxidation can also lead to a change in the emission wavelength. Reducing CDs with sodium borohydride causes a blue shift in emission, while oxidation with sodium acetate causes a red shift in emission wavelength. Reduced CDs generally have a narrower bandwidth compared to their oxidized counterparts.

Likewise, the adsorption pattern of CDs depends on their structure. The array of the graphitic core with π-conjugation facilitates π-π* transitions, while the lone pair of electrons on oxygen and nitrogen atoms allows n-π* transitions. Therefore, the overall structure, particularly the surface functional groups, significantly influences the optical behavior of CDs. In general, CDs tend to aggregate when the target molecule coordinates with their surface functional groups. This coordination induces favorable changes in surface functional groups, enhancing fluorescence [75].

3.3 Quantum confinement

These CNPs can function as artificial antennae, enabling chloroplasts to capture light wavelengths beyond their usual range, including ultraviolet, green, and near-infrared light. One of the most intriguing features of Carbon Dots (CDs) is their tunable photoluminescence (PL), where their emission peak can be adjusted from deep ultraviolet to the visible region. These tunable PL properties are closely related to CDs' quantum confinement effect or surface effects. The photoluminescence of CDs is believed to originate from emissive surface energy traps upon stabilization, which is essential for achieving high quantum yield in PL CDs.

Furthermore, CDs have demonstrated superior performance in various physiological processes of plants, such as growth, photosynthesis, and resistance to abiotic/biotic stress [76-78]. Additionally, CDs treatments have shown enhanced effects on biological nitrogen fixation by azotobacter [79].

4. Artificial photosynthesis

CDs have been employed as agents to enhance growth in crop systems by facilitating photosynthesis. This involves applying synthesized CDs of specific sizes onto plants, where the leaves absorb them. This interaction leads to heightened sunlight and carbon dioxide absorption rates due to the presence of CDs [80]. Consequently, the photosynthesis process accelerates, potentially resulting in a crop growth and production increase ranging from 10% to 20%. In this section,

we will delve into the process of photosynthesis to convert solar energy, CO_2, and H_2O into fuels and oxygen and how CDs offer promising opportunities for efficient and sustainable artificial photosynthesis.

The light absorption capability of CDs has artificial light-harvesting antennae for photosynthesis across the UV and visible light spectra. In the natural process the photosynthesis, plants employ chloroplast pigment to capture solar light and convert it into carbon dioxide resulting in carbohydrates, ATP, and oxygen. Mostly the efficiency of photosynthesis is only dependent on the chloroplast's limited ability to absorb light, with approximately 10% of the total solar energy received being absorbed. Chlorophyll, the primary pigment, absorbs light in the blue and red regions of the visible spectrum only ranging from 400 nm to 700 nm [81].

A growing requirement for finding new strategies that will enhance the chlorophylls' light-absorbing properties to improve photosynthesis and crop yield is the possibility of shifting the absorption into a wider range. A recent trend in the field of nanomaterial/chloroplast hybrid systems has attracted much attention for their ability to boost light absorption abilities. For this purpose, carbon dots (CDs) present themselves as good candidates due to their ability to capture energy from UV and visible excitation ranges. Several current studies advocate CDs as synthetic antennae that augment photosynthesis capacity by trapping more light.

CDs have received much attention in the literature as blue emissive CDs for light harvesting; however, it is important to consider the role of long-wavelength red and far-red emissions in artificial photosynthesis. In photosynthesis, plants can take advantage of wavelengths such as far-red directly. When dealing with traditional blue-emitting CDs, it may be difficult to differentiate between CD emission and chloroplast fluorescence. Thus, there is increasing interest in investigating far-red CDs as potential light-harvesting antennae that can absorb UV light and convert it into far-red light (emitted at 625 nm to 800 nm), which is also absorbed by chloroplasts.

The increased electron transfer between Photosystem II and Photosystem I lead to increased ATP production. The incorporation of CDs in the role of light-harvesting antennae for photosynthesis is still a fairly new idea that is currently being studied deeply and in detail [81-86].

Furthermore, carbon dots (CDs) exhibit disease-resistance properties that safeguard plants against various diseases [87]. Li *et al*. conducted research employing CDs to investigate their impact on plant growth and disease resistance in rice crops [87]. Their findings demonstrated the remarkable ability of CDs to efficiently infiltrate all parts of the rice plants, including cell nuclei. By densely loading CDs into plants, there was a substantial enhancement in seed germination, root growth, leaf count, and enzymatic activity, facilitating the conversion of CO_2 into carbohydrates through accelerated photosynthesis. As a result of these effects, rice crop production saw an impressive increase of up to 14.8%. Additionally, the CDs conferred a disease-resistance capability that shielded the plants from damage [75]

5. Advantages of CDs in artificial photosynthesis

Carbon dots (CDs) find remarkable applications across various domains not solely due to their inherent attributes but also their capability to interact synergistically with other nanoscale materials possessing exceptional qualities. This results in the creation of nanohybrids with amplified overall characteristics. Typically, the primary focus centers on crafting CDs nanohybrids with inorganic nanoparticles like iron oxide, zinc oxide, titania, and silica. These resultant CDs nanohybrids amalgamate the qualities of both CDs and the inorganic nanoparticles, introducing novel attributes. Consequently, these nanohybrids hold significant potential across diverse fields such as electronics, efficient photocatalysis, biosensing, and beyond [88].

In a study conducted by Pandiyan, S. *et al*., carbon quantum dots (CQDs) were tested for their antibacterial properties against both Gram-positive and Gram-negative bacteria. The experiments demonstrated that CQDs can hinder bacterial growth, supported by the size of zones of inhibition (ZOIs) observed in the tests. The antibacterial effect is thought to be due to functional groups present in the CQDs that interfere with bacterial enzyme functions and hinder cell proliferation. The CQDs have a large conjugated carbon system and can easily attach to bacterial cell walls through electron transfer as shown in Figure 14.

Previous studies of Pandiyan, S., *et al*., (2020) have also reported nitrogen-containing CQDs with proven antimicrobial effects against both Gram-positive and Gram-negative bacteria [89]. Specific CQDs synthesized in this study showed higher inhibition rates against Bacillus cereus, Staphylococcus aureus, Pseudomonas aeruginosa, Vibrio cholera, and Escherichia coli than other CQDs. As a result, of these newly synthesized CQDs hold potential for use in pharmaceutical applications due to their demonstrated antibacterial properties (Pandiyan, S., *et al*., 2020).

In another study by Li *et al*. (2022), CDs' quantum yield (QY) was investigated for its influence on plant growth and yield. The researchers proposed that CDs notably augmented the leaf count and expanded the leaf surface area by increasing leaf width, concurrently fostering root growth [85]. The impact of CDs' concentration on the yield and morphology of lettuce, as well as macroscopic observations of the shoot [90].

In a study by Wang *et al*. (2018), the impact of various concentrations of carbon dots (CDs) solutions (ranging from 0 to 0.12 $mg{\cdot}mL^{-1}$) on the growth of mung bean sprouts over six days was investigated [77]. Another study conducted by Zheng *et al*. involved the use of hydrothermally synthesized CDs derived from rapeseed pollen. In this research, the effects of different concentrations of CDs (ranging from 0 $mg{\cdot}mL^{-1}$ to 30.0 $mg{\cdot}mL^{-1}$) were studied concerning lettuce plant growth parameters. The results showed that the concentration of 30.0 $mg{\cdot}mL^{-1}$ of CDs had the most pronounced positive effect on aspects such as vegetable growth indices, photosynthetic pigment content, overall quality, and morphological characteristics. This concentration demonstrated the highest efficacy in promoting increased plant yield.

For instance, Hazarika *et al*. devised a CD@TiO_2 nanohybrid through hydrothermal treatment involving titanium butoxide and environmentally friendly carbonaceous materials like cow urine, glycerol, and citric acid. This produced a highly efficient photocatalyst displaying exceptional pollutant degradation proficiency for substances like phenol, benzene, and pesticides [91].

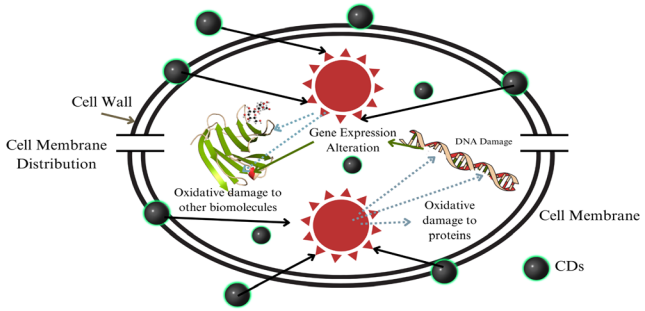

Figure 14. Schematic Diagram of the Antimicrobial Activity Mechanism.

6. Challenges

The integration of carbon dots (CDs) into artificial photosynthesis for agricultural applications presents a promising avenue to address food security and sustainability challenges. However, this endeavor is not without its complexities. One of the foremost challenges lies in optimizing the efficiency of CDs as photosensitizers in the artificial photosynthesis process. While CDs offer exceptional photoluminescence properties, their effectiveness in capturing and converting light energy into chemical energy must be fine-tuned to match the demands of agricultural systems.

Moreover, achieving stable and efficient catalytic activity for carbon dioxide reduction using CDs remains a significant hurdle. The conversion of carbon dioxide into useful compounds such as carbohydrates demands precise control over reaction kinetics and product selectivity. Developing CDs with the right surface chemistry and catalytic properties to facilitate this transformation is a multifaceted challenge that requires a comprehensive understanding of both material science and agricultural biochemistry.

Furthermore, the scalability of the artificial photosynthesis approach with CDs is a critical concern. Moving from laboratory-scale experiments to real-world agricultural settings requires the production of CDs on a larger scale while maintaining consistent quality and performance. Overcoming this challenge necessitates advancements in CDs synthesis methods and the development of cost-effective, environmentally friendly production processes.

7. Future perspectives and potential applications

Looking ahead, the potential of utilizing carbon dots in artificial photosynthesis for agriculture applications is nothing short of transformative. The marriage of nanotechnology, sustainable agriculture, and renewable energy holds immense promise. CDs' unique optical properties can be harnessed to efficiently capture sunlight across a broad spectrum, enhancing the overall efficiency of the artificial photosynthesis process. Their compatibility with biological systems also positions them as excellent candidates for integration into living plant tissues, further optimizing light absorption.

In the context of agricultural productivity, the integration of CDs could revolutionize crop yields. By bolstering the energy conversion efficiency of plants, artificial photosynthesis with CDs might enhance their growth rates and nutritional content. The resulting increase in agricultural productivity has the potential to mitigate food scarcity and bolster global food security, a critical concern in a world grappling with a growing population and changing climate patterns.

Beyond immediate crop yield enhancements, CDs might also enable the development of hardier and more resilient plant varieties. The ability to fine-tune CDs' properties could lead to plants that are better equipped to withstand environmental stresses such as drought, salinity, and extreme temperatures. This facet of CDs' potential aligns with the imperative of adapting agriculture to climate change and ensuring sustainable practices for the future.

8. Conclusion

In the pursuit of sustainable agricultural practices, the intersection of carbon dots and artificial photosynthesis emerges as a beacon of hope. While challenges in efficiency optimization, catalytic activity, and scalability exist, they are met with the collective ingenuity of scientists, engineers, and agricultural experts. The potential rewards of this endeavor are substantial and far-reaching.

The prospect of leveraging CDs' unique properties to drive artificial photosynthesis holds promise not only for increased crop yields but also for the mitigation of environmental impact. As agriculture grapples with the dual challenge of feeding a burgeoning global population while preserving natural resources, the integration of CDs into this paradigm has the potential to strike a harmonious balance between productivity and sustainability.

The journey ahead involves collaborative efforts across disciplines, from nanotechnology and chemistry to agronomy and renewable energy research. As advancements continue to be made in CDs synthesis, surface modification, and catalytic mechanisms, the vision of harnessing CDs for artificial photosynthesis in agriculture applications draws closer to fruition.

In conclusion, the potential of carbon dots in artificial photosynthesis for agriculture applications underscores the power of innovation to reshape fundamental practices. Challenges, although significant, are poised to be surmounted through persistent research and technological advancements. The future holds a landscape where CDs not only contribute to higher crop yields but also play a pivotal role in sustainable agriculture, ultimately nourishing both the planet and its inhabitants.

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