Carbon Dots: Synthetic Routes, Optical Properties, and Emerging Applications

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Abstract

Carbon dots (cds) have been an emerging carbon-based nanomaterial that has drawn attention due to their facile synthesis, distinct optical properties, and diverse applications. The synthesis of new carbon dots by various techniques including electrochemical oxidation, microwave treatment, and laser passivation that allow control of size, surface passivation, and emission behavior. Carbon dots manifest optical properties such as absorbance in the ultraviolet region and luminescence mechanisms, including photoluminescence, phosphorescence, chemiluminescence, and electrochemical luminescence which are of importance in sensing, imaging, and catalysis. The various applications of carbon dots are increasingly being explored more in diverse applications that include bioimaging, catalysis in hydrogen peroxide generation, in solar cells, drug delivery systems, light-emitting diodes. Cds, recognized for their excellent biophysical properties, present an appealing alternative to traditional quantum dots and organic dyes in applications ranging from biology to environmental science. The potential of cds, enabled by their simple synthesis and low levels of toxicity, currently extends to many other applications, such as biomedical, and optoelectronic, necessitates exploring the synthetic strategies, optical characteristics, and emerging applications of cds for their optimal utilization within scientific research and various technologies.

Keywords: Carbon dots, Quantum dots, Optical properties, Nanomateials, Photocatalysis

1. Introduction

In 2004 during the purification of carbon nanotubes a spherical particle with zero dimension of size less than 1nm were discovered. The carbon nanodots (cnds) consist of sp^2 or sp^3 hybridization of carbon atom (Zhang *et al.*, 2018). Comprising discrete, quasi-spherical nanoparticles, cds represent a novel class of carbon nanomaterials. They were originally identified in 2004 when purifying single-walled carbon nanotubes from the constituents of fluorescent nanoparticles. These nanoparticles of carbon were known as "carbon quantum dots" until 2006. Since then, cds have drawn a lot of attention because of their distinctive structure and intriguing properties in a variety of sectors. Being one of the new carbon allotropes, cds exhibit several impressive properties, including excellent photoinduced electron transfer, stable chemical inertness, low cytotoxicity, and good photocompatibility. As a result, they are promising candidates for a variety of roles in biosensors, biological imaging, optical electronics, solar cells, and other fields.

It is widely known that there are three primary types of carbon dots: carbonized polymeric dots (cpds), graphene quantum dots (gqds), and carbon nanodots (cnds). In general terms, carbon dots are just tiny carbon nanoparticles within aqueous or other fluids. The sizes of π-conjugated domains and their arrangements on their surfaces or edges have a major impact on the optical properties of gqds (Xia *et al.*, 2019). This material with anisotropic properties comprises nano-sized graphite in single or multiple layers, along with surface or edge functional groups and interlayer defects. Its lateral dimensions surpass its height.Unlike gqds, which feature a spherical nucleus connected to surface groups, both cqds and cpds lack this arrangement. The photoluminescence (PL) emission properties of cqds are chiefly governed by their intrinsic luminescent state and the quantum confinement effect arising from their size. Their spherical core displays multiple-layer graphite architectures. Cross-linked and aggregated carbon cores with polymer chain shells make up cpds, which are hybrid nanostructures (Mansuriya and Altintas, 2021). The optical attributes of cpds are chiefly affected by their molecular configuration and interconnection pattern.

The most convincing point of carbon nanodots is its synthetic approaches which are facile and in which inexpensive precursors are used. Due to these characteristics, carbon nano dots are used in various fields like biomedical imaging,

photovoltaic panels, photocatalysis, drug delivery, sensors and many others(Asadzadeh-Khaneghah *et al.*, 2020). The core of carbon nanodots could be partially crystalline or amorphous. The diverse configurations of the cds are influenced by different synthesis methodologies, which can be broadly categorized into "bottom-up" approaches and "top-down" approaches .The top down method is used for the making of crystalline carbon nano dots from graphene which is referred to as gqds (Hu *et al.*, 2021). However, many crystalline graphene carbon cores are also obtained by bottom up synthetic routes. Therefore, most of the researchers preferred to name them as carbon quantum dots which is also used for the amorphous carbon dots (Habibi-Yangjeh *et al.*, 2020).

The surface functional groups of cds can be changed by utilizing various synthesis procedures, which will result in adjustable light emission. More specifically, the modified surface moieties comprising cds facilitate the expansion of the light utilization range from different states of emissive traps due to their efficient up-converted photoluminescence conduct. This implies that it is possible to develop effective cds that respond to visible light over the entire spectrum of sunlight. (Cui *et al.*, 2021). Moreover, the cds-based composites' capacity to capture light helps to enhance photoexcited electron transfer, which raises photocatalytic efficiency.

In light of the systematic summary provided on the synthesis routes, properties, and applications of cds, we seek to present a distinct perspective by compiling a comprehensive review of recent progress in CD research. Our focus will be on highlighting the latest advancements in cds, emphasizing their synthesis, properties, and applications. Specifically, we will begin by summarizing various cost-effective and environmentally friendly synthesis routes for producing cds from diverse sources, particularly natural biomass. Following this, we will delve into the optical properties of cds. Finally, we will discuss the fundamental roles and potential developments of cds as photocatalysts in photocatalytic systems.

2. Synthesis Approaches

On the basis of starting carbon source, the synthetic routes for cnds are classified into two major categories including bottom up and top down approaches. The small molecules like glucose and citric acid as precursor are used in bottom up method for the synthesis of carbon nano dots. While we

use a bulk material like graphene, carbon fiber and graphite are used in top down method (Zhou *et al.*, 2017). However, cds are synthesize by both top down and bottom up methods as shown in **figure 1**. For the improvement of emission properties of carbon dots like photo stability, wavelength of emission and quantum yield, the doping of heteroatoms have been applied for the surface passivation during the synthesis of cnds. The choice of the carbon dots synthesis is depend on the requirement and applications because different type of carbon nano dots exhibit opposite properties (Wang *et al.*, 2009).

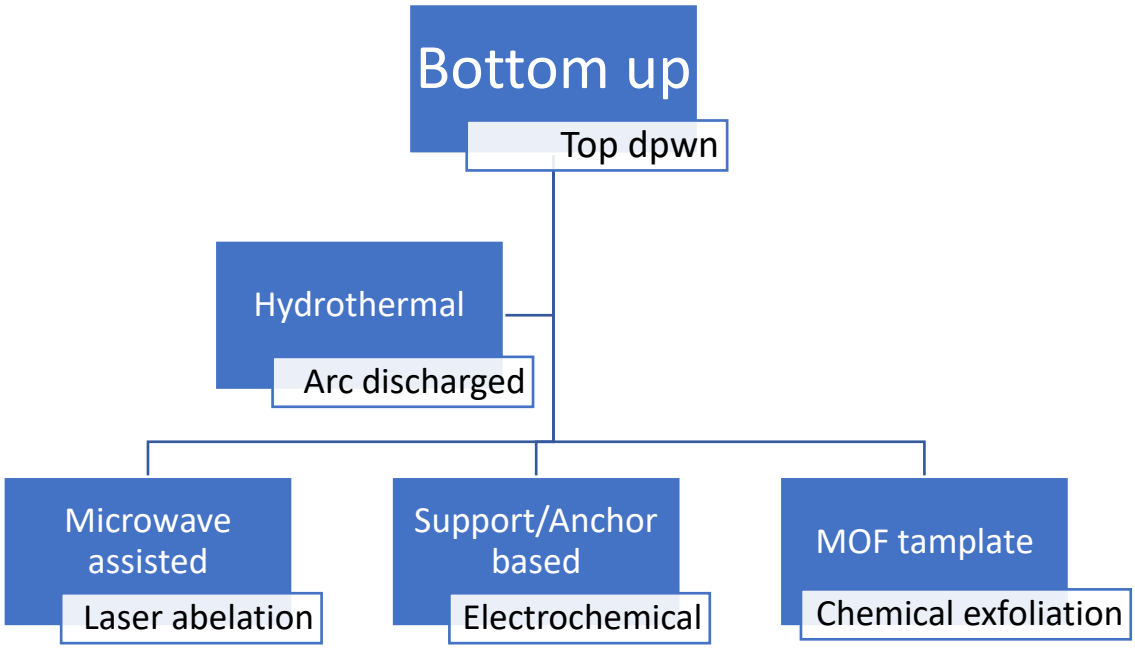

Fig. 1 Synthesis Routes for Carbon Nano Dots: Bottom-Up vs. Top-Down Approaches

2.1 Bottom-up Approaches for the Fabrication of Carbon Nanodots

The bottom-up synthesis of carbon nanodots encompasses diverse methodologies aimed at precisely constructing these nanostructures from molecular or atomic precursors. This multifaceted approach includes hydrothermal and microwave-assisted methods, harnessing controlled conditions to foster the growth of nanodots. Additionally, the Support/Anchor-based and MOF template-assisted approaches offer innovative strategies, leveraging solid supports or intricate frameworks to guide the formation and organization of carbon nanodots with tailored properties and functionalities.

2.1.1 Hydrothermal Method

In 2011, the hydrothermal method was used for the synthesis of cnds. A certain molar ratio of monopotassium phosphate and glucose were mixed and dissolved into deionized water. For the removal of oxygen, the nitrogen has been employed (Yang, 2011). After this an autoclave chamber with Teflon lining was shifted to the oven for 12 hours at 200℃. The centrifugation of the mixture was done at 9000rpm for the separation of precipitate. The precipitate was collected and freezing dried, carbon dots dissolved into the ethanol which give rise to a suspension (De and Karak, 2013). The salt would precipitate out after standing for 2hr and filtration done by Polytetrafluorethylene (PTFE) syringe of pore size 1µm. Further purification was done by dialysis membrane. The whole process is summarized in **figure 2**.

The formation of carbon dots cds and treatment of its surface are the major advantage of this method because they are accomplished simultaneously (Wang and Zhou, 2014). By altering the concentration of monopotassium phosphate (KH_2PO_4), the photoluminescence properties would be altered. By the excitation of UV light, a green emission caused with molar ratio of 1/26 of glucose/monopotassium phosphate of carbon dots. While the blue light emitted when the molar ratio of glucose/monopotassium phosphate was 1/36 of carbon dots (Wang and Zhou, 2014). The transmission electron microscopy (TEM) analysis was result in 3.38nm in diameter for green carbon nano dots and 1.83nm diameter for blue carbon nano dots. The Fourier transform infrared spectroscopy (FTIR) was analyzed the presence of carbonized carbon nano dots by hydrothermal synthesis. By the oxidation of hydroxyl group (-OH), the surface passivation has been occurred. The other natural bio sources like orange juice have been utilized for the carbon dots synthesis but relatively at low temperature round about 150℃ (Holá *et al.*, 2017).

The organic components when undergo hydrothermal carbonization like glucose, fructose, juice of orange and citric acid caused the emission of carbon nano dots. The transmition electron microscopy (TEM) analysis gave spherical morphology with 1.5nm and 4.5nm in diameter of carbon nano dots (cnds).Different hydrophilic functional groups, such as -COOH and -OH, were found using infrared spectroscopy with Fourier transform analysis, indicating that carbon nanodots have good water solubility (Ren *et al.*, 2018).

The formation of carbon nano dots followed by the major steps including dehydration, polymerization, carbonization and passivation. The assembling of molecules by polymerization give nucleation growth in which hydrogen bonding played a key role (Wang *et al.*, 2014). Through the nucleation, the solute molecules of nuclei reached to the surface by diffusion which gave growth to the carbon dots. The synthesis of cnds whose emission wavelengths cover the entire visible spectrum are possible by adjusting the reaction environment i.e. Acidic or basic or choosing proper organic molecules with controlled surface passivation through hydrothermal process (Pan *et al.*, 2010).

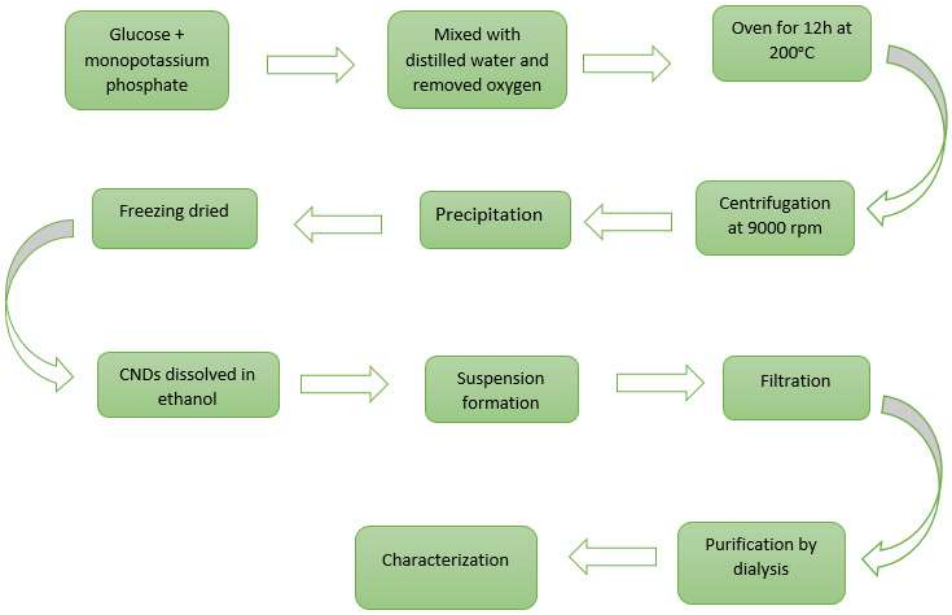

Fig. 2 Flowchart illustrating the synthesis process of carbon nanodots via the hydrothermal method.

2.1.2 Microwave Assisted Method

Scientists discovered the carbon nano dots by using microwave assisted method which is facile, cost effective and consumes less time. The saccharides like fructose and glucose and polyethylene glycol were mixed in deionized water to form transparent solution (Zhu *et al.*, 2009). The solution kept in microwave for 2 to 10 minutes at power 500W as shown in **figure 3**. When the solution turned into dark brown color than the carbon nano dots were formed. With the varying of reaction time, the diameter of cnds

was different (Zhai *et al.*, 2012). The X-ray photoelectron spectroscopy (XPS) analysis result containing carbon and oxygen as major components of carbon dots with hydrophilic functional groups which showed excellent water solubility and biocompatibility. The photoluminescence of carbon nano dot's quantum yield told us that the green emission gave high quantum yield and blue emission gave relatively low quantum yield (Chandra *et al.*, 2011).

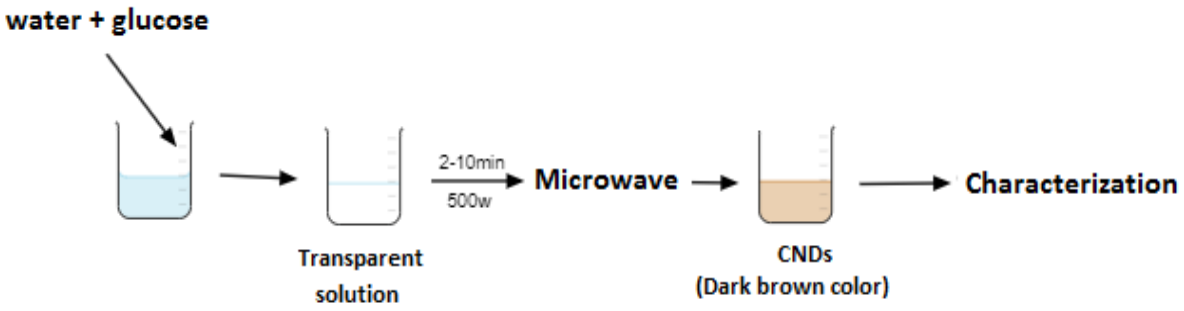

Fig. 3 Synthesis process of carbon nanodots via the microwave assisted method.

2.1.3 Support/anchor-based Approach

Liu's group have been employed silica spheres for the synthesis of cnds. The polymerization of carbon source accelerated by silica spheres which act as anchor or support. During pyrolysis at high temperature the aggregation of cnds was caused suppression by the silica sphere. The surface of silica firstly treated with amphiphilic triblock copolymer (F127) which is requirement for the synthesis of cnds (Liu *et al.*, 2009). On the surface of sphere, the micellization which is self-assembly of molecule triggered by the surfactant F127. The interaction of water and surfactant caused extension of the sphere's surface which result in the surfactant structure of core shell silica-F127. For the loading and polymerization of molecules, the opened shell of F127 contributed for the pass of the carbon dots into the shell layer (Wang *et al.*, 2018). The hydrophilic part of the amphiphilic triblock copolymer (F127) play more anchored part of the molecule and have strong interaction of hydrogen bonding which result in the creation of polymer/F127 surfactant/silica sphere composites. After all the surfactant treatments the source of carbon was added for the polymerization (Bourlinos *et al.*, 2008).

The calcination method has been used for polymer/F127/silica structure for 2hrs at

900℃. The argon gas was used as protection gas. During calcination the surfactant F127 was fully released. By the etching process with sodium hydroxide (naoh), the carbon nano dots was released from the silica sphere (Gu *et al.*, 2017). To achieving bright photoluminescence was still crucial for the passivation of surface. The heating of solution of carbon nano dots with diamine terminated oligomeric poly ethylene glycol was done at 120℃ for 72 hours which was carried out for the post surface treatment. The whole method is summarized in figure 4. The Energy-dispersive X-ray (EDX) analysis showed that carbon 64.65 % weight, nitrogen 1.13% by weight, hydrogen 7.67% by weight and oxygen 26.55% by weight. The average diameter size of the particle was in between 1.5nm-2.5nm. The excitation light source at 360nm gave emission of photoluminescence of quantum yield 14.7% (Xu *et al.*, 2015). The sodium yttrium zeolite has also been used as support for the synthesis of cds . However, the carbon dots with support and without support showed similar photoluminescence properties (Amali *et al.*, 2014). The entire synthesis process is depicted in **Figure 4**, showcasing the sequential steps involved in achieving carbon nanodots with desired properties.

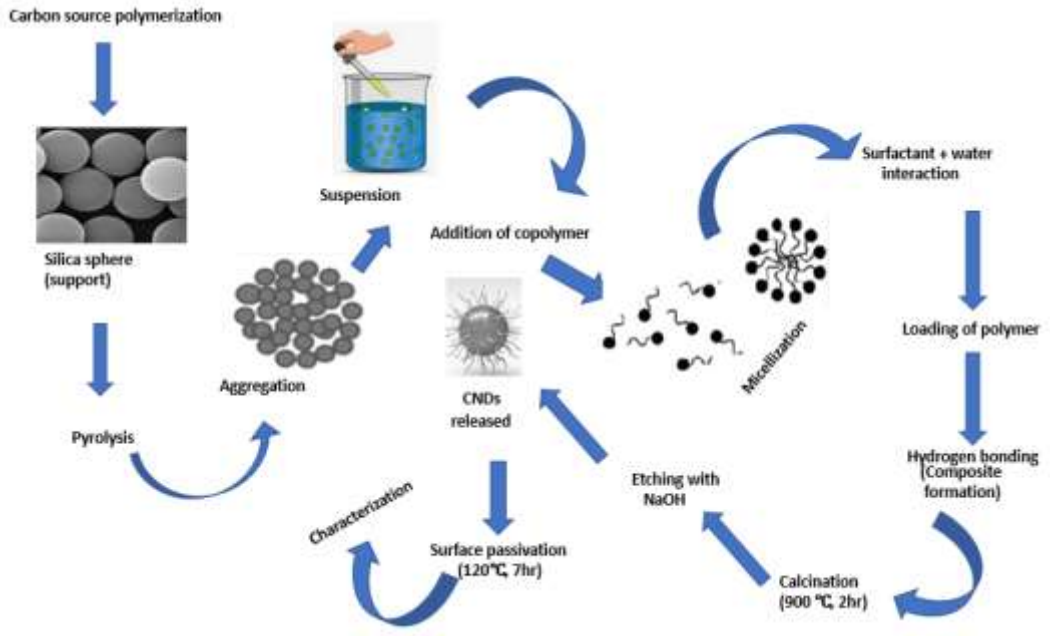

Fig. 4 Schematic Representation of the Synthesis Process for Carbon Nanodots Utilizing the Support/Anchor-based Approach

2.1.4 MOF Template-based Approach

The metal organic frameworks (mofs) was used by Zhi-Gang Gu and coworkers for the synthesis of cnds of uniform size. The mofs were beneficial due to their pore size which was vary from 1nm-10nm in diameter size that was suitable for the synthesis of cns of controlled size and morphology. The hydrothermal method was used for the synthesis of mofs (Gu *et al.*, 2017). The dipping of MOF pallets into the mixture of ethoxide/water and glucose was loaded inside the MOF pore. The successful loading of the sample confirmed different weight of the HKUST-1MOF samples before 1 g and after 1.13 g. When loading material was heated at 200℃., the glucose started to decompose while MOF template remained stable which was confirmed by the thermogravimetric method (Xu *et al.*, 2015). The structure of MOF did not destroy during calcination which was confirmed by the Powder X-ray diffraction (PXRD) analysis. The color changed from blue to green which was indication of cnds presence. The calcinated MOF caused considerable decreasing in adsorption of nitrogen from 130 cm3/g – 5 cm3/g which was the conformation of filling of MOF pore by cnds (Amali *et al.*, 2014).

The Solution of potassium hydroxide dissolved the MOF template and cnds was released. The purification of cnds showed narrow pore size which was contained average 1.5nm diameter. This synthesis process is summarized in **Figure 5**, showing the sequential steps involved in fabricating cnds with tailored properties and functionalities. The different pore size of the template also helped to synthesize the different sizes of cnds (Yang *et al.*, 2013). The synthesized cnds with average diameter of 4.5nm was contained non regular size distribution. The red shift results from photoluminescence of cds which showed that the size of cnds increased from 1.5 nm - 4.5 nm by ultraviolet light. The controllability of cnds size and morphology gave hard template and soft template which developed uniformity in the morphology of cnds (Huang *et al.*, 2018).

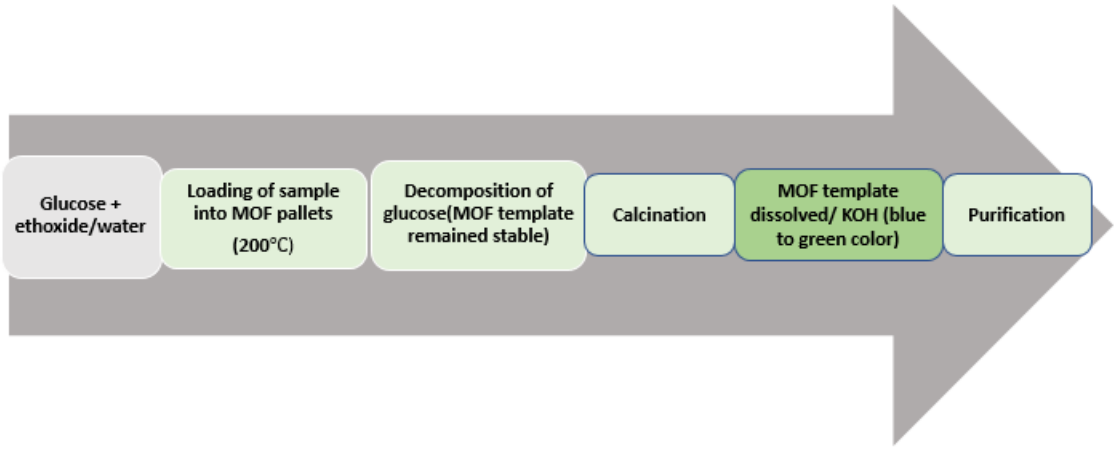

Fig. 5 Schematic representation of the Template-based Approach for synthesizing cnds using mofs. The sequential steps include precursor loading into MOF pores, template dissolution with KOH, and the transformation of MOF templates into purified cnds with precise size distributions.

2.2 Top down Approaches for the Fabrication of Carbon Nanodots

To implement top-down techniques, a bulk carbon source, like graphite, carbon fiber, and graphene, is directly exfoliated into nano-scale carbon dots, then the surface is treated. By starting with larger carbon sources and employing various techniques to disintegrate and refine them at the nanoscale, top-down approaches offer versatility in synthesizing carbon nanodots for various applications.

2.2.1 Arc Discharged Method

In 2004, the purification of single walled carbon nanotubes soot was done by preparative electrophoresis method. The three kind of nanotubes i.e. Short nanotubes, long nanotubes and other one located at the fast-moving band after purification. The carbon nano dots could emit light under 365nm. The separation of mixed fluorescence by elution gave the presence of yellow, orange, blue and green sub emission bands. The molecular weight of three different nano tubes included 3K to 10K, 10K to 30K and 30K to 50K nominal molecular weight limit by centricon filtration device. The EDX analysis showed that nanotubes contained hydrogen as 2.65%, nitrogen as 1.2%, carbon as 55.93%, and oxygen at 40.33%.There were no indication of heavy metal components in the elemental analysis (Xu *et al.*, 2004).

2.2.2 Laser Ablation/ Irradiation Method

In 2006, Sun et al. Suggested a novel method for producing fluorescent carbon-

based nanostructures, sometimes known as cds. A carbon target which was fabricated with cement and hot pressing of graphite has been ablate by Q-switched Nd: YAG laser of 10Hz and 1064nm. The acidic treatment for refluxing 12 hours was done with 2.6 M nitric acid solution. There was no detection of photoluminescence emission after acidic treatment of sample (Sun *et al.*, 2006). The bright luminescence could be observed when we connected surface of cnds with simple molecule as summarized in **figure 6**. For the passivation of surface, the poly (propionyl ethyleneimine-co-ethylene imine) and diamine oligomeric poly (ethylene glycol) could be used. In the treatment of surface passivation, the mixture of small molecules i.e. Oligomeric molecules and carbon nano particles was heated for 72hrs at 120°C (Wang *et al.*, 2015). The bright photoluminescence of carbon nano dots was observed with average diameter of 5nm and containing 10% quantum yield when excited by 400nm laser. The varying of wavelength, the photoluminescence spectra would also be changed. However, carbon nano dots exhibit stable emission for several hours under continuous photoexcitation. The amendment approach of combining surface modification and laser ablation, the pulsed laser of Nd: YAG of wavelength 1.054μm for the irradiation of organic solvent and mixture of graphite give cnds formation and modified surface. The emission properties of cnds can be adjusted by changing organic solvents (Wang *et al.*, 2016).

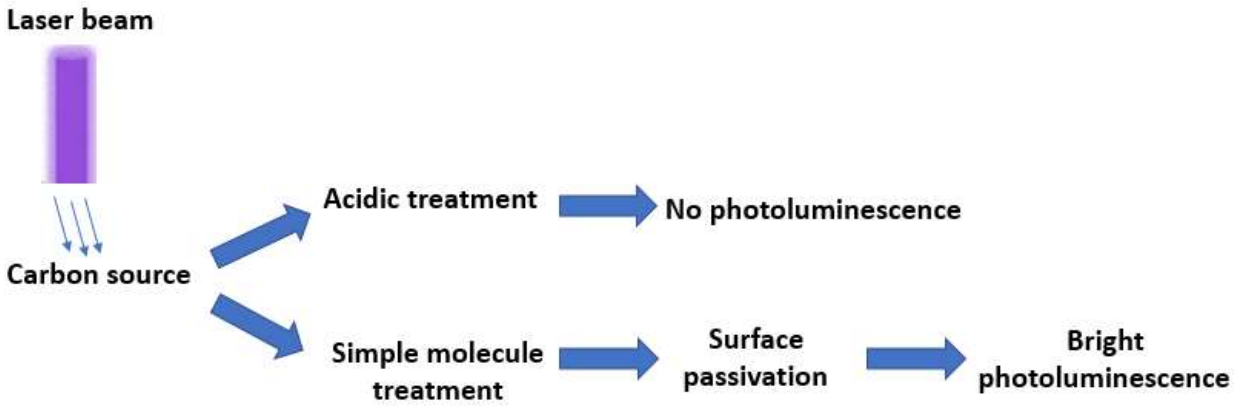

Fig. 6 Carbon target is subjected to laser ablation, acid treatment, and surface passivation using polymers and oligomeric molecules. The resulting cnds exhibit bright photoluminescence with tunable emission properties.

2.2.3 Electrochemical Method

Ding's group first synthesize the cnds from multi walled carbon nano tubes (mwcnts). By using chemical vapor deposition method (CVD), the fabrication of mwcnts was done by scrolling graphene layer on carbon paper. This was utilized as the working electrode in an electrochemical cell together with an $Ag/agclo_4$ reference electrode and a platinum wire counter electrode (Zhou *et al.*, 2007). The solution of acetonitrile degassed contained 0.1M tetrabutylammonium perchlorate which supported electrolyte solution. The solution was changed from colorless to dark brown after applied potential of -2V to 2V for certain cycles which was the indication of presence of cnds. By evaporating the acetonitrile, the purification of cnds was done and re-dissolved in water. The dialyzing was done by cellulose ester membrane bag (Li *et al.*, 2010). The purified cnds with lattice spacing about 3.3 Å which shown average diameter size of 2.8nm±0.5 nm. The quantum yield of 0.064 was obtained when the carbon nano dots emitted blue bright light by exciting 340 nm light source (Zhao *et al.*, 2008).

Li and coworker also working on the synthesis of cnds by using graphite as both cathode and anode. The current intensity would be ranged between 10 to $200ma/cm^{-2}$. The electrolytic environment played a significant role in the formation of cnds. The acidic environment (H_2SO_4/etoh) could not synthesize cnds while the basic environment (naoh/etoh) successfully form the cnds. The transmission electron microscopy (TEM) analysis had revealed the lattice spacing of 0.32 nm with diameter of 4 nm (Bao *et al.*, 2011).

2.2.4 Chemical Exfoliation Method

Cnds was first discovered by Liu and coworkers by employed oxidative acid from bulk candle soot which was obtained from smoldering candles. The 5M HNO_3 was used for refluxing than followed by centrifugation and neutralization (Liu *et al.*, 2007). For the purification and separation of different component of sooth mixture, the polyacrylamide gel electrophoresis was used. The soot mixture was contained of three species included slow moving fluorescent, fast moving fluorescent and agglomerate band (Hu *et al.*, 2009). The fast-moving band was subdivided further into nine bands which were located at various position of the column. The dialysis was done for several times after eluted from gel. The cnds had 1 nm height which was analyzed by Atomic force microscopy (AFM). The different

column band of cnds had different emission spectra (Strauss *et al.*, 2014).

Cnds was also synthesized by Ajayan's group from carbon fiber. For the exfoliation of carbon fiber, the mixture of ammonium nitrate (HNO_3) and Sulphuric acid (H_2SO_4) was prepared. The carbon fiber added to the conc. Acid which sonicated for 2 hours. The mixture was heated for 24 hour at certain temperature with constant stirring. The synthesized cnds were exhibited 1-4 nm in diameter with 0.242 nm lattice parameter. By controlling the reaction temperature, the photoluminescence and absorption properties could be tuned which yield various kind of cnds (Zhu *et al.*, 2013).

3. Optical Properties of Carbon Nanodots

The most exciting feature of cnds is their optical properties like excellent photostability, reflected by the ph variation and excitation dependence. Cnds surface passivation with different semiconductor quantum material which on substitution make them effective for the removal of contaminants from water. These tunable cnds are widely used in bioimaging, photocatalysis, sensing and bio medical applications like drug delivery. Cnds most of the time showed green and blue photoluminescence emissions (Khan *et al.*, 2021). Now they cover the entire visible region of electromagnetic spectrum.The highest quantum yield of cnds was observed as 80% and most of the cases also gave below 10% of the quantum emission. Cnds sometimes also show a characteristics of low energy photons to emit high energy emission (upconversion). Cnds photoluminescence emissions originates from conjugate structure, edge effects, quantum effects, surface states and free zigzag sites. The addition of heteroatoms to cnds attribute in the formation of broad spectra which may due to the surface state of carbon nano dots (Manisha *et al.*, 2019). Therefore, it is very important to obtained efficient cnds with smooth and uniform size.

3.1 Absorbance

Cnds exhibit absorbance in ultraviolet region with tail ranging towards visible region. The absorption behavior of carbon dots (C-dots) primarily arises from the transition of electrons within the π molecular orbitals of the carbon framework, known as the π–π* (pi-pi*) shift of double bonds (Li *et al.*, 2016). This transition leads to the absorption of light in the short-wavelength region of the electromagnetic spectrum. The cnds specially synthesized by electrochemical oxidation, microwave or ultrasonic, laser passivation and metal

supported method showed absorption in between 260 nm-320 nm. However, by the surface passivation of carbon nano dots we could increase to the longer wavelength i.e. 350 nm-550 nm for trioxa-1,13-tridecaneduamine and 340 nm-360 nm for organ silane.

3.2 Photoluminescence (PL)

In optical properties small sized cnds, the most striking feature is PL mechanism which depend on the surface passivation, size of the particles, intensity and wavelength emission. The surface passivation of cnds directly related to its synthetic route. Only some certain methods show the bright PL which exhibit broader spectra from visible region to near infrared region. The wavelength emission is varying with the difference in size of cnds. The optical behavior of cnds no only depend on size of the particle but also on the different emissive sites on each cds.

Sun et al., had studied the surface traps of cnds which reflect the emissive upon surface passivation. He observed that to exhibit bright and strong PL there must be a quantum confinement effect of emissive energy traps on the surface (Hu *et al.*, 2019). This similar effect was revealed in silicon nano crystals. The passivation of cds coated with zinc oxide or zinc sulphate was done by using PEG1500N for the PL to occur. However, nanocomposites like copper, palladium, silver of cnds synthesized by the use of oxidized gas soot required no passivation for PL, its only mandatory for the cnds which prepared by the supported method (Schwenke *et al.*, 2015).

3.3 Phosphorescence

The optical shift from a triplet state (T_1) into the singlet state which is the ground state (S_0) is referred to as phosphorescence. This process is spin-forbidden(Baryshnikov *et al.*, 2017). The lifespan of phosphorescence is greater than the duration of fluorescence. Cds have been studied as a new optical response material. Their room temperature phosphorescence has been observed using both time-resolved phosphorescence spectroscopy and steady-state PL spectroscopy. The excitation of triplets is facilitated by the triple bond between carbon and nitrogen bonds. Additionally, the complex matrix played a crucial role in preventing the nonradiative processes, which prevented the triplet state from being quenched during its long period. Water molecules have been employed alongside organic molecules to form hydrogen-bonded networks with cds, facilitating phosphorescence emission. The

resulting hybrid of cds and cyanuric acid (CA) exhibited an extended phosphorescence lifetime of 687 milliseconds, attributed to the heightened rigidity of the cds following the addition of CA (Li *et al.*, 2023).

Phosphorescence energy transfer systems involving cds and inorganic matrices due to their potential applications in sensing and security. One notable example is the observation of phosphorescence energy transfer between carbon nanotubes and Mn-doped zns quantum dots linked with capture single-stranded DNA (ssdna), enabling highly sensitive DNA detection. Apart from the polymers, organic molecules, and functional inorganic matrix, room-temperature phosphorescence has also been reported in individual cds (Hildebrandt *et al.*, 2017).

3.4 Chemiluminescence (CL)

CL is the process by which photons are released from excited states into ground states in a chemical reaction. Most of the features of CL are comparable with the characteristics of fluorescence. While the energy that causes the emission of fluorescence comes from outside light sources, the activation potential of CL is produced by self-chemical processes. In a chemical reaction, a molecular unit or an atom gains energy by the absorption of chemical energy that's generated during the process. Optical radiation is released when the charged molecule or atom recovers to its ground state. Because there is no external light source present, CL remarkable property typically exhibits a high sensitivity. The study on CD-based CL analysis is still in its early stages at present (Liu *et al.*, 2019).

The CL properties of cds were investigated in a solution containing $nano_2$ and H_2O_2, where cds were identified as the primary emitters in the cds–$nano_2$–H_2O_2 system. Analysis of CL spectra revealed that the systems comprising $nano_2$ + H_2O_2 and cds + H_2O_2 exhibited weak CL emissions individually, whereas the system involving $nano_2$ + H_2O_2 + cds displayed significantly stronger CL emissions. This observation suggested that the product generated (oxidant, ONOOH, and OH_3) during the reaction of nitrites and acidified H_2O_2 facilitated the transformation and injection of small holes into the cds (Shen *et al.*, 2020). This process accelerated hole-injected annihilation and increased the number of injected electrons, leading to the release of energy in the form of CL emissions.

It has been noted that the surface functionalities of cds significantly influence

their CL properties. For instance, the CL intensity of cds synthesized in peroxynitrite was found to be correlated with the concentration of C–O group-associated O-states. This suggests that cds with abundant C–O functional groups and high O-states tend to facilitate electron transfer, thereby enhancing CL intensity.A recent study shows that nitrogen-doped graphene quantum dot (N-gqds) significantly increase the CL strength of the permanganate-sulfite system. Interestingly, the enhancement mechanism for N-doped gqds was found to be independent of particle size. CL spectra analysis revealed that pyridinic nitrogen in N-gqds acted as a catalytically active site for amplified CL emission(Muthurasu *et al.*, 2018) . Furthermore, an increase in pyridinic nitrogen concentration led to a corresponding enhancement in CL intensity.

3.5 Electrochemical luminescence (ECL)

To investigate the fluorescent properties of semiconductors, nanocrystals and cds, the ECL is extensively used. The behavior of cnds is alike to the silicon crystals and quantum dots in ECL. The ECL explained the reduced state and oxidized state of the cnds which result in annihilation transfer of two oppositely charged carriers and formation of excited state (Mehta *et al.*, 2023). By emitting a photon, the excited cds returned to the ground state in radiative pathway. The cathodic ECL was less than the value of anodic which showed that the reduced state was more stable than oxidized state. With passage of time the electrochemical response was relative stable which is very useful for the sensing application. The ECL of semiconductor nanomaterials was red shifted due to the surface defects in the band gap (Arcudi, 2017).

The comparison of PL and ECL is the method used to investigate surface traps. A helpful technique to determine whether nanoparticles have surface traps is to analyze their ECL as well as PL. This is because, although PL appears more descriptive of the core state within nanoparticles, ECL is primarily linked to interface-state changes in nanoparticles. According to a theory put forth by Baker et al., the core band gaps of C-dots are size-dependent, with the least intense bands potentially due to surface-state traps, and the strongest band being caused by direct recombination of electron holes. This hypothesis was based on the ECL evidence for the presence of surface trap states and the pervasive size- and lex-dependency of C-dot PL. Determining whether the ECL of C-dots is size-independent would also be fascinating (Kang *et al.*, 2012).

4. Applications of cnds

4.1 Bioimaging

With significant benefits including substantial PL quantum yields, photo-stability, durability against metabolic degradation, and more, cds set themselves apart from fluorescent chemical dyes and genetically engineered fluorescent proteins. These attributes endow the enormous potential of carbon dots-based bio-applications (Du *et al.*, 2019). Using PEG1500N as a surface passivation agent, researchers assessed the in vitro toxicity of cds created by laser ablation of graphite fines and cement using human colorectal adenocarcinoma HT-29 cells and human breast cancer MCF-7 cells , even though the toxicity evaluation of cds is necessary and the prerequisite for investigating the bio-applications of cds (Sulaiman *et al.*, 2023). Cds showed superior biocompatibility, according to all the observations of cell growth, mortality, and viability from the two cell lines, even at concentrations of up to 50 g/ml, which is significantly greater than what is necessary for practical applications like living cell imaging. Furthermore, researchers also performed an in vivo toxic evaluation using male CD-1 mice. Carbon dots were intravenously injected into the two groups of mice at concentrations of 8 mg/kg and 40 mg/kg, respectively (Dhamodharan *et al.*, 2022). A 0.9% sodium chloride aqueous solution injection was given to the next group of mice as a safe control injection. Throughout the four weeks of the experiment, every mouse exhibited typical behavior; neither aggressive nor indolent behavior was seen (Xu *et al.*, 2020).

According to histopathological analyses, cds would not change the liver, spleen, or kidney sections' anatomical makeup. Without a doubt, the results above demonstrated that cds are safe to use in both the in vitro and in vivo settings. Similar results from the zebrafish research were also observed, along with the evaluation in mice, indicating the high biocompatibility of cds. Additionally, scientists verified that the cds—which were created by heating urea along with citric acid in a microwave—hurt biological architecture. A 1.5 mg/ml water-based solution containing cds was used to cultivate bean sprouts. The findings demonstrated that plant cells were able to absorb cds and produce bright, emissive bean sprouts. Furthermore, there was no indication of any overt toxicity or inhibition of plant growth (Kasouni *et al.*, 2019). Moreover, the features cnds and their benefits in bioimaging are shown in table 1.

Table 1: Features of cnds and their benefits in bioimaging

Features of cnds	Benefits in Bioimaging	Examples	References
Fluorescence	On excitation, release a range of hues of light, serving as probes for cellular imaging.	Cell labeling to monitor particular cell types	(Chatzimitakos *et al.*, 2023)
Biocompatibility	Less hazardous than conventional quantum dots, making them safer to utilize in biological applications	Allows in vivo imaging with few risks to health	(Babu *et al.*, 2021)
High Water Solubility	Easy incorporation into biological systems	Promotes cellular absorption in order to detect biomolecules	(Khan *et al.*, 2021)
Surface Functionalization	Focusing on particular biomarkers within cells to provide focused imaging	Targeted binding allows for the detection of particular biomolecules	(Kishore *et al.*, 2023)
Tunable Size and Properties	Customizable optical characteristics and targeting capabilities	Customizing cnds to meet certain imaging requirements, such as deeper tissue penetration	(Atchudan *et al.*, 2020)
Photostability	Improved image quality and a longer signal duration are guaranteed	Allows for the long-term observation of biological processes	(Du *et al.*, 2020)

Cds are regarded as having a natural place in bio- and clinical applications due to their exceptional biocompatibility and vivid brightness. The ground-breaking study on cds bio-imaging was carried out. First, laser-produced carbon dots were used. The E. Coli ATCC 25922 cells were labelled by laser ablation, and the cells changed color as the excitation wavelength changed. The in vivo imaging of cds was later demonstrated by the same group e-i. 30 g of cds (dissolved in 30 l of water) were subcutaneously injected into

the female DBA/1 mice (25 g). The mice that had received injections under their skin had intense green emission (da Silva and Gonçalves, 2011).

4.2 Catalysis

Using glucose and a combination of glucose and glutamine in an ionic liquid (1-ethyl-3-methylimidazolium ethyl sulfate), cds were created. To assess the impact of the nitrogen doping on the oxidation reactions, bare cds were also created using glucose as the sole precursor. After being exposed to radiation for various durations, the two distinct precursor mixes were dialyzed to produce cds that were B12 nm in size (Singh *et al.*, 2018). In all instances, the cds surface moieties of -COOH, -OCO, -CQN, and -NH_2 suggested the development of N-doped dots, as would be expected given the presence of the imidazoline ring.

The final product was used as an independent catalyst to selectively oxidize oxygen molecules, resulting in the production of hydrogen peroxide. The oxidative reduction process may have occurred in two stages, with H_2O_2 acting as an intermediate, based on the presence of both reduced processes detected by voltammetry with linear sweeps (LSV), which was utilized to assess the catalysts' effectiveness. When the amount of H_2O_2 generated was plotted against potential, it became evident that, at 0.3 V, the greatest amount (94%) was created along with a decrease in the counting of electrons (Chen *et al.*, 2020).

The fact that the undoped cds did not produce much H_2O_2 indicates that the atoms of nitrogen had a big influence on the mechanism (Haidri *et al.*, 2023). Yet further research is necessary to understand the precise nature of how this mechanism works. These outcomes are quite encouraging because the obtained cds demonstrated good stability and effectiveness as reducing agents (Sharma and Das, 2019). Due to their ability to mix the distinct qualities of their constituent parts, hybrid materials can offer a number of benefits. Scientist created a CD/tio_2 composite that is N-doped for use in photocatalytic processes as a result. To generate the cds, glycerol, ammonium phosphate and TTDA (4,7,10-trioxa-1,13-tridecanediamine) were reacted in a microwave-assisted process (at a power of 700 W), for 7 min. The obtained materials were cleaned up using dialysis, resulting in nanoparticles having -COOH, -OH, -NH_2 and -NCQO moieties on the surface that were B9 nm in size. The reaction of tio_2 (P25) with the derived cds in water, with hydrothermal assistance, at 130 °C for 4 hours, produced

the hybrid material. The production of the tio_2/N-doped cds composite and the emergence of the Ti-O-C bond in the spectrum of X-ray photoelectron spectroscopy (XPS) were both confirmed by TEM pictures. According to thermogravimetric measurement, the hybrid system's CD content was roughly 0.69 percent. The UV degradation of methylene blue (MB) and a control consisting of a physical mixture of P25 and the cds were then used to examine the photocatalytic assessment of the cds. When compared to control and pure P25, the composite's degradation ratio was 2.35X greater. This was mostly ascribed to the N-doping moieties that are present on cds and can change the bandgap of tio_2, as well as acting as electron acceptors and transporters, lowering the recombination ratio and encouraging oxidative processes (Dhenadhayalan *et al.*, 2020).

4.3 Solar cells

Solar photovoltaic cell research has been accelerated by the never-ending search for clean, renewable energy sources. These cells are a significant new use for cds and an increasingly attractive alternative to fossil fuels. Their relatively poor conversion efficiency, or their capacity to convert photons into current, is one of the main shortcomings of solar cells (Pal *et al.*, 2020). Although solar cells conversion efficiency has been gradually increasing over time, significant improvements must yet be made before they can be a practical substitute for non-renewable energy sources. In order to increase conversion efficiency, solar light absorption or charge transport (CT) have both been increased. The complexity of these devices has increased along with the utilisation of rare or dangerous substances as a result of numerous advancements. So, there is a demand for a more safe, affordable, scalable, and accessible CT material. Cds are strong candidates to boost the efficiency of solar cells due to their chemical stability, electrical capabilities, and metal-free nature (Feng *et al.*, 2020).

Dye-sensitized solar cells (dsscs) are solar cells that contain dyes that, when connected by oxide electrodes, produce current in the cell with electrochemical activity. They aimed to create and enhance carbon dot-sensitized solar cells (cdsscs) in order to reach an efficiency comparable to the performance for quantum dot-sensitized solar cells (qdsscs). It was proposed that a lack of understanding of cds' electrical structures, non-optimized electrolytes, and insufficient photoelectrode insurance were the main causes of cdsscs' subpar performance.

Consequently, technologies that improve device assembly and a novel synthesis methodology that allows the absorption of a greater amount belonging to the visible spectrum were introduced (Essner and Baker, 2017). For this, cds were created using a citric acid, urea, and formic acid solution in water in a regular microwave oven. The synthesized cds, depending on the mole ratio of the precursors utilized, showed a broad range absorbance up to 700 nm, a polydisperse distribution of sizes with a slight bimodality, and an excitation-wavelength relationship. (de Medeiros *et al.*, 2019).

Reduced ph increased electrode coverage, which promoted the production of photocurrent and elevated the efficiency of solar cells. It was suggested that this resulted from cds being more protonated, which would decrease their dispersibility and hence increase their absorptivity (Langer *et al.*, 2021). The protonation of tio_2 increased its hydrophilicity and permitted better mesoporous network penetration. On the other hand, It was observed that while low energy photons transmit electrons to tio_2 inefficiently, cds performance did not improve with their absorption range expanded. (Akbar *et al.*, 2021).

4.4 Drug delivery

For carbon dots to be suitable for in vivo bioimaging applications, it is crucial that they exhibit excellent biocompatibility and can be effectively removed from the body. Theragnostic nanomedicine is made possible by the theragnostic function cds' bright emission makes it feasible for tracking distribution of drugs and response dynamically and in real-time. Groups, which include amino, carboxyl, hydroxyl, and others and are abundant and tunable (Tuerhong *et al.*, 2017). Oxaliplatin, one of the numerous platinum-based medications, is carried on cds created by thermal pyrolysis for citric acid as well as polyene polyamine. More than 40% of clinical patients with cancer receive platinum-based drugs as part of their chemotherapeutic regimen, which are the most effective anticancer treatments available. To create CD-Oxa, one of the derivatives of oxaliplatin (IV), Oxa(IV)-COOH, was utilized to bond with cds. An interaction between the activating COOH pair of Oxa(IV)-COOH and the groups of amino acids on the cds' surface completed the connection. (Dugam *et al.*, 2021).

The effective attachment of Oxa(IV) to carbon dots was confirmed by the recently observed Pt 4f XPS signal. According to an ICP-MS (Inductively coupled plasma mass spectrometry) examination, the platinum

element in cds-Oxa was 1.5 weight percent, or 4.2 weight percent oxaliplatin (IV). Also, according to TEM data, the diameter of cds-Oxa (2.71 0.43 nm) was bigger than that of pure cds (2.28 0.42 nm) (Tao *et al.*, 2017). Using intralesional injection, synthetic cds-Oxa was administered to Chinese Kun Ming (KM) mice with hepatocarcinoma 22 cell line (H22) liver cancer. The drug's dynamic distribution was then monitored using an in vivo optical imaging system with blue light serving as the excitation source. Due to the high concentration of cds at the time of exposure, a highlight point was visible from in vivo imaging (Liu *et al.*, 2016). The subsequent delivery of cds-Oxa caused the fluorescence intensity to drop from its original position and spread the intensity distribution. The PL signal significantly decreased at 24 hours post-injection, indicating that the amount of oxaliplatin (IV) was diminishing. As a result, the researchers administered a second injection, and the PL intensity increased once more (Huang *et al.*, 2013).

Researchers also created charge-convertible cds for medication delivery (Feng *et al.*, 2016). While the ph was 7.4-normal for physiological conditions—the carbon dot surface was negatively charged; however, as the ph dropped to 6.8, it became positively charged, simulating the microenvironment of a tumor. By preventing normal cells from absorbing drugs due to the attraction of electrostatic charge between the negative-charged cds interface and the negatively charged membrane of the cell, the negatively charged cds surface in the normal cell microenvironment lessened the side effect. On the other hand, due to their electrostatic interaction with the negatively charged cell membrane, the positively charged cds found on surfaces in the microenvironment of malignant cells may facilitate the intake and absorption of cancer-specific treatments. Conversely, due to their electrostatic interaction with the negatively charged cell membrane, the positively charged cds surface in the microenvironment of tumor cells may facilitate the absorption of anticancer drugs.Based on both in vitro and ex vivo research, cds have the potential to be a useful image-guided medicine delivery system with lower side effects and higher therapeutic efficacy (Jiang *et al.*, 2021).

4.5 leds

Achieving direct white light emission from cds in 2010, researchers opened the door to the creation of cds-based devices that emit white light. Later, the cds emitting white light were used as emissive layer while the construction of the white light emitting

devices. Citric acid was used as a source of carbon along with 1-hexadecylamine which was used as the passivation agent of the surface during the thermal pyrolysis process to manufacture cds. (Sharma *et al.*, 2018). This process produced cds average diameter of 5 nm and a relatively high quantum yield of 60%. The device's architecture consisted of three layers. 40 nm poly (3,4-ethylenedioxythiophene):
poly(styrenesulfonate) (PEDOT: PSS) on anode served as the buffer layer and have two purposes. First, it Boost the work-function to 5.0 ev from 4.7 ev and secondly improve the anode's smoothness. The spun-cast method was used to create the cds emissive layer, which has an ideal thickness of 20 nm. The density of porosity and boundaries of grains, etc., will grow with a thinner covering, like one of 10 nm. While a thicker film, such as one of 35 nm, will result in poor charge transport in the cds film, both of which will reduce the EL efficiency of the device. The CD film's surface roughness was measured using an Atomic force microscopy (AFM) and found to be less than 3 nm, indicating high compatibility between the cds and the buffer layer (Ashok *et al.*, 2020). Because to its reliable electron transport capabilities, 1,3,5-tris(Nphenylbenzimidazol-2-yl)
benzene (TPBI), which has a thickness of 40 nm, served as the layer for the transit of electrons.

When the voltage was raised to 10 V, the LED device showed stable emission, while the pure carbon dots showed widespread PL with an emission feature (Yuan *et al.*, 2017). The light that was released had the Commission International d'Eclairage (CIE) coordinates of (0.40, 0.43) ((0.33, 0.33) for pure white light), and it had a Color Rendering Index (CRI) of 82. The maximum external quantum efficiency (EQE) of the White Light-Emitting Diode (WLED) was 0.083% at a current density of 5 ma/cm^2, and the maximum brightness output was 35 cd/m^2 at a current density of 160 ma/cm^2 and voltage of 9 V. The WLED had a turn-on voltage of 6 V. High energy emission relaxation process was quicker. High injection current levels can stimulate all three emission bands, whereas low injecting current densities cause the heated particles to relax via the rapid decay channel, leading to high power emission, including the 412 nm band or blue emission. Furthermore, in the case of a significant current injection, the lower band emission will predominate because the densely packed excited states can feed the lower emission band, which includes the 480 nm and 580 nm wavelength states.

The scientists were able to achieve the tunable colour emission based on one type of cds by altering the injection current. Indium Tin Oxide (ITO) anode, 25 nm hole injection layer, 40 nm hole transport layer (HTL), 20 nm carbon dots layer, 5 nm electron transport layer (ETL), and top cathode layer were the six layers that made up the LED. As the hole injection layer, poly (ethylenedioxythiophene): sulfonate (PEDOT: PSS) has been used. The adoption of poly-(N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl) benzidine) (poly-TPD) as the HTL was made possible by the material's better hole transport properties, matched energy alignment with the PEDOT:PSS layer, and ease of uniform thin film synthesis (Yan *et al.*, 2015). The ETL and the cathode layer were designed with particular functions in mind. As previously stated, varying injection current density (or the matching applied voltages) will result in varying emission colors.

A low current injection density was required to produce pure blue emission CD leds, so they increased the thickness of the lif layer of the cathode layer from 1 nm to 5 nm (Qu *et al.*, 2019). As a result, the current density dropped to 150 ma/cm^2, producing pure blue CD leds with a turn-on voltage of 5 V and a maximum luminance of 24 cd/m^2. Likewise, the white light emission could be caused by high current density injection. Since the cathode layer only contained 150 nm of aluminium, zno nanoparticles were used as the ETL. The high electron mobility of zno nanoparticles (2*10-3 cm^2 V-1 S-1 for zno, compared to 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl) benzene (TPBI) 1*10-4 cm2 V-1 S-1) provided the emissive layer with a high injection current density, which led to the emission of white light. The white CD LED's maximum brightness was 90 cd/m^2 and its turn-on voltage was around 4.6 V (Biçer, 2023). Researchers have suggested using cds having emissions in addition to varying the amount of injection current density to create monochromatic light-emitting leds.

Hydrothermal processes were used to create the cds. All the blue, green, yellow, orange, and red emission cds have been produced by carefully managing the carbon supply (citric acid), nitrogen source (2,3-diaminonaphthalene or 1,5-diaminonaphthalene), surface passivation/carbonization (concentrated sulfuric acid), and reaction time. The quantum yield of all the cds was relatively high: 75% (B), 73% (G), 58% (Y), 53% (O), and 12%. (R). The cds EL spectra were in agreement with their PL spectra and showed

voltage independent EL hues with peaks at 455 nm (blue), 536 nm (green), 555 nm (yellow), 585 nm (orange), and 628 nm (red) (Shamsipur *et al.*, 2017). The band emission of cds with the quantum confinement effect for the voltage stable EL emission as well as the controllable PL emission. The CIE coordinates, maximum luminance, current efficiency for the monochrome leds were ((0.19, 0.20), 136 cd/m^2, 0.084 cd/A), ((0.31, 0.47), 93 cd/m^2, 0.045 cd/A), ((0.37, 0.52), 60 cd/m^2, 0.02 cd/A), ((0.46, 0.48), 65 cd/m^2, 0.027 cd/A), ((0.55, 0.41), 12 cd/m^2, 0.0028 cd/A) for blue, green, yellow, orange, and red leds respectively (Lagonegro *et al.*, 2020).

Conclusion and Future Perspective

The primary focus of this study is on the latest developments in cds production, optical characteristics, and applications, particularly in the areas of drug administration, biosensors, and biological imaging. Numerous synthesis techniques have been thoroughly examined; the advantages include large-scale manufacturing, low cost, and ease of availability. With their low cytotoxicity, excellent photoinduced electron transfer, and effective light harvesting, the produced cds are very advantageous and adaptable materials for drug administration, biological sensors, and in vitro bioimaging. Despite tremendous efforts, there are still several obstacles in the way of creating multipurpose cds with a predetermined structure.The chemistry of reaction precursors, reactivity factors, and measurable reaction indicators are just a few of the numerous variables that make the controlled preparation of cds a critical problem that needs to be resolved. Furthermore, most cds ultraviolet absorption restricts their use, particularly in bioimaging. As a result, making cds with larger wavelengths is going to be a popular area for research. Even though the difficult tasks mentioned above are still ongoing, the field of cds has advanced significantly in recent years. In terms of both fundamental research and real-world applications, the future of cds appears bright.

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