Review

Preparation methods, properties of carbon quantum dots, and their advanced applications

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Article Information

Abstract

Carbon quantum dots (CQDs) have emerged as a versatile class of nanomaterials due to their unique optical, chemical, and biological properties. This essay explores the synthesis methods of CQDs, categorized into top-down and bottom-up approaches, including techniques such as laser ablation, electrochemical synthesis, hydrothermal, and microwave irradiation methods. The optical properties, including absorbance, photoluminescence, and fluorescence, are discussed alongside their chemical inertness and adsorption capabilities. Advanced characterization techniques, such as mass spectrometry, spectroscopy, microscopy, and diffraction, are reviewed for their role in understanding CQD structure and functionality. The essay further delves into CQD applications in environmental monitoring, bioimaging, optoelectronics, and cancer treatment, with a focus on photodynamic therapy, photothermal therapy, and drug delivery. By highlighting their biocompatibility and tunable properties, this work underscores the transformative potential of CQDs in addressing critical challenges in healthcare and environmental sustainability.

1. Introduction

In the rapidly evolving field of nanotechnology, CQDs have emerged as a revolutionary class of nanomaterials, captivating researchers with their remarkable optical, chemical, and biological properties. These tiny carbon-based particles, typically less than 10 nanometers in size, have garnered significant attention due to their unique ability to combine fluorescence, biocompatibility, and chemical stability. Their tunable properties, achieved through diverse synthesis methods and surface modifications, make them highly versatile for applications ranging from environmental sensing to advanced medical therapies. This essay explores the synthesis, properties, and transformative applications of CQDs, highlighting their potential to address pressing global challenges[1, 2].

The development of CQDs has been propelled by the establishment of efficient synthesis techniques, broadly categorized into top-down and bottom-up approaches. Top-down methods, such as laser ablation and electrochemical synthesis, involve breaking down larger carbon structures into nanoscale dots, while bottom-up methods, like hydrothermal and microwave irradiation techniques, build CQDs from smaller molecular precursors[3]. Each method offers distinct advantages in controlling size, morphology, and surface chemistry, which are critical for tailoring CQDs to specific applications. For instance, doping with heteroatoms like nitrogen or phosphorus enhances their solubility and electrical conductivity, broadening their utility in fields such as optoelectronics and bioimaging. The flexibility of these synthesis methods has

enabled CQDs to become a customizable platform for cutting-edge technological advancements[4, 5].

The optical properties of CQDs, including their absorbance, photoluminescence, and fluorescence, are central to their widespread appeal[6]. These properties, which can be fine-tuned through surface passivation and doping, enable CQDs to emit vibrant light across the visible and near-infrared spectrum, making them ideal for fluorescence-based applications. Beyond their optical allure, CQDs exhibit exceptional chemical inertness and adsorption capabilities, allowing them to interact effectively with various molecules and ions. Their biocompatibility and low toxicity further enhance their suitability for biological applications, such as drug delivery and cancer therapy, where they outperform traditional semiconductor quantum dots. These characteristics position CQDs as a powerful tool in both scientific research and practical applications[7, 8].

The applications of CQDs span a diverse array of fields, from environmental monitoring to healthcare and energy-efficient technologies[9]. In environmental science, their fluorescence properties enable the rapid detection of pollutants like heavy metal ions, offering a sustainable solution for contamination control. In medicine, CQDs serve as fluorescent probes for bioimaging and as carriers for targeted drug delivery, particularly in cancer treatments like photodynamic and photothermal therapies. Additionally, their integration into optoelectronic devices, such as solar cells and light-emitting diodes, underscores their potential to drive energy innovation. The ability to characterize CQDs using advanced techniques like mass spectrometry and microscopy ensures precise control over their properties, further expanding their practical utility[5, 10].

The purpose of this essay is to provide a comprehensive overview of carbon quantum dots, detailing their synthesis methods, unique properties, and wide-ranging applications, while highlighting their potential to revolutionize fields such as healthcare, environmental sustainability, and optoelectronics. By examining the interplay between their synthesis, characterization, and functionality, this work aims to underscore the transformative impact of CQDs and inspire further research into their untapped potential.

2 .Synthesis methods

Various efficient methods for producing CQDs have been developed since their discovery. These methods are easy, cost-effective, allow for size control, and enable large-scale manufacturing. The synthesis of CQDs involves two main approaches: top-down and bottom-up. While the synthesis of CQDs is relatively easy, there are specific difficulties associated with their production, including the tendency of nanomaterials to aggregate, the need to adjust surface qualities, and the control of size and homogeneity. In order to enhance the performance of CQDs, post-treatment may be carried out using one of the two techniques to modify the functional groups on the surface. The quantum yields (QYs) of CQDs may be increased by surface passivation, which removes the emissive traps present on the surface. CQDs that have been doped with heteroatoms such as nitrogen (N) and phosphorus (P), or metals like gold (Au) or magnesium (Mg), exhibit enhanced solubility and electrical conductivity. Although both the top-down and bottom-up methodologies have been used for the synthesis of CQDs, the bottom-up strategy, which is environmentally friendly and cost-effective, is the most widely employed method[11].

2.1 .Top-Down Approach

Using a top-down approach, various techniques such as laser ablation, electrochemical methods, and arch discharge are employed to break down larger carbon resources like carbon nanotubes, fullerene, graphite, graphene, carbon soot, and activated carbon into smaller components.Carbon structures exhibiting sp2 hybridization and lacking effective energy gaps or band gaps are often used as initial materials for top-down procedures. While the top-down approach is beneficial and appropriate for microsystem industries, it has limitations. One such

limitation is the inability to obtain pure nanomaterials directly from the large carbon precursor. Additionally, the purification process is expensive and does not allow for precise control over the morphology and size distribution of CQDs [12, 13].

2.1.1 .Laser Ablation Method

In 2006, Sun and his colleagues were the first to introduce a laser ablation technology. This process involves the synthesis of CQDs by exposing a target surface to a high-energy laser pulse. Li et al.[14] recently produced ultra-small CQDs of consistent sizes utilizing the laser ablation technique. They used fluorescent CQDs for the purpose of cell imaging applications. Cui et al.[15] have successfully produced uniform CQDs using a rapid and highly effective dual-beam pulsed laser ablation technique. These CQDs are intended for use in bio-imaging applications and exhibit high quantum yields (QYs). In addition, Buendia et al.[16]used laser ablation methods to produce fluorescent CQDs that were utilized for cell labeling. The CQDs produced using this method often lack fluorescence, exhibit size variability, and have a poor quantum yield, which impacts their prospective uses. Hence, in order to enhance the fluorescence characteristics and quantum efficiency, it is necessary to carry out pre-treatments such as surface passivation (doping) and oxidation.

2.1.2 .Electrochemical Method

Zhou et al.[17] first documented the electrochemical technique. The researchers used a tetra-butyl ammonium perchlorate solution as the electrolyte to create the first blue luminous CQDs from multiwall carbon nanotubes (CNTs). This approach involves the electrochemical oxidation of larger carbon precursors in the presence of a reference electrode, resulting in the fragmentation of the precursors into smaller components. Zhao et al.[17] fabricated fluorescent carbon nanomaterials by electrochemical oxidation, using a graphite rod as the working electrode . Zheng et al. [18]created water soluble CQDs that can emit light of different colors by utilizing graphite as an electrode material and adjusting the pH using . Deng and his colleagues synthesized the CQDs from low-molecular-weight alcohol using the oxidation technique. They suggest that the most direct and easiest method to produce CQDs is by doing the process at normal atmospheric pressure and temperature [19]. In 2015, Hou and his colleagues produced highly luminescent blue-emitting CQDs by subjecting urea and sodium citrate to electrochemical treatment in de-ionized water [20]. The electrochemical approach has many advantages, such as the absence of surface passivation, cheap cost, and a straightforward purification procedure [11]. Nevertheless, this method's drawback lies in its restriction to a limited number of molecular precursors for the synthesis of CQDs, as well as its laborious purification procedure. Thus, it is the approach that is utilized the least often [11].

2.1.3 .Arch Discharge Method

Fluorescent carbon quantum dots were first serendipitously discovered by Xu and colleagues while separating and purifying a single-wall carbon nanotube using the arch discharge technique. Nitric acid was used as an oxidizing agent to oxidize arch ash, resulting in the formation of various functional groups on the surface. This led to an increase in water solubility. QYs achieved were 1.66% when excited at a wavelength of 366 nm [21]. A further experiment revealed that the surface of CQDs was bound to hydrophilic carboxyl groups. During the discharge process, carbon particles of varying sizes are generated. The approach yields CQDs that exhibit great water solubility and a broad range of particle sizes. In addition, a technique called electronic flash was used to distinguish fluorescent nanomaterials from both pure carbon nanostructures and carbon nanostructures that had been oxidized with nitric acid [22].

2.2 .Bottom-Up Approach

Through a bottom-up methodology, several processes such as hydrothermal/solvothermal, combustion, pyrolysis, and microwave irradiation are used to mix smaller carbon resources including amino acids, polymers, carbohydrates, and waste materials in order to create CQDs. The size and structure of CQDs in this process are influenced by many parameters, including

the solvent, precursor molecule structures, and reaction conditions (such as pressure, temperature, and reaction time). The reaction conditions are essential as they impact both the reactants and the very spontaneous nucleation and growth process of CQDs. This strategy enhances the material chemistry due to its simplicity of usage, reduced expenses, and more convenient use for large-scale manufacturing[23] .

The precursor used for the synthesis of CQDs might be of both chemical and biological nature, namely, natural. The chemical precursors consist of glucose, sucrose, lactic acid, ascorbic acid, citric acid, glycerol, ethylene glycol, and others[24-29] .The natural sources of the substance include seeds of *Artocarpous lakoocha*, rice husks, leaves of *Azadirachta indica*, peel of pomelo, latex of *Ficus benghalensis*, *aloe vera*, etc. (see Figure 1)[30-32] .

2.2.1 .Hydrothermal Method

Zhang et al. [33] first disclosed the hydrothermal approach for synthesizing CQDs using l-ascorbic acid as the carbon source, without the need for any chemical reactions or surface passivation. The synthesized CQDs had an average size of around 2 nm, and the resulting QY was 6.79%. Four distinct solvents (water, acetone, ethyl acetate, and ethanol) were used in the synthesis of vivid blue emission CQDs. It was noted that the CQDs that were soluble in water exhibited remarkable stability at room temperature for a duration of 6 months. Furthermore, the fluorescence intensity of CQDs remained constant throughout a broad pH range and in highly ionic salt conditions (2 M NaCl). During the hydrothermal process, the molecules that come before the final product are dissolved in water. They are then put in a Teflon-lined stainless-steel autoclave and transferred to the hydrothermal chamber. The chamber is set at high temperature and pressure for a few hours .The precursor molecules used for synthesis include proteins, polymers, amino acids, polyols, glucose, some wastes, and natural products [34]. The hydrothermal technique has gained significant global interest in recent years because to its simplicity, convenience of use, lack of toxicity, affordability, and environmental friendliness. CQDs produced using hydrothermal treatment has many advantageous characteristics. These include great uniformity, solubility in water, uniform distribution, resistance to degradation by light, tolerance to salt, regulated size of particles, and a high quantum yield without the need for surface passivation. In addition to the hydrothermal approach, the synthesis of CQDs also involves the use of a solvothermal process, which employs ammonia, alcohol, and other organic and inorganic solvents instead of water [35, 36].
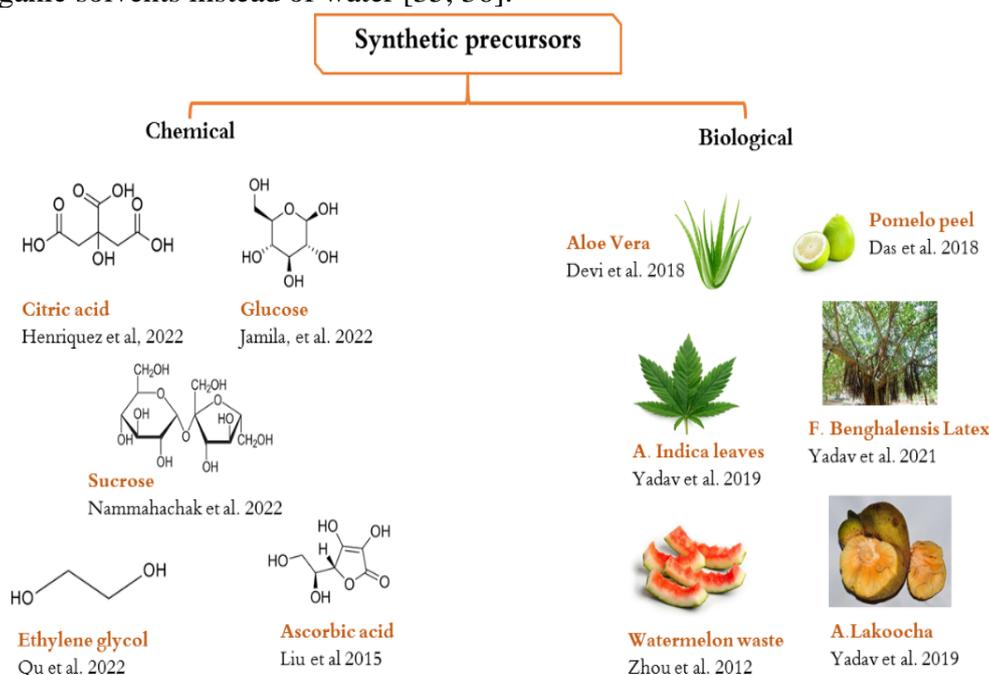

Fig.1 Chemical and biological substances used in the production of CQDs[31, 32, 37-39] .

2.2.2 .Combustion Method

Liu et al.[40] first documented the use of the combustion technique for synthesizing CQDs. This technique utilizes oxidative acid treatments to combine tiny carbon resources into CQDs, improve their solubility in water, and regulate their fluorescence characteristics.Liu et al.[40]clarified that candle ashes were acquired by the incomplete burning of a candle using aluminum foil, followed by refluxing it in a solution of nitric acid. The pure CQDs were produced by dissolving the candle ashes in a neutral solution, followed by centrifugation and a dialysis procedure. The CQDs produced by the combustion approach had a low QY but demonstrated satisfactory fluorescence in the absence of doping [30].

2.2.3 .Pyrolysis Method

Pyrolysis is a process in which a precursor is thermally decomposed at a high temperature (usually over 430 °C) and under pressure, without the presence of oxygen. In the presence of an alkali and high acid concentration as a catalyst, the carbon precursor undergoes cleavage, resulting in the formation of nanoscale colloidal particles. This approach has many favorable qualities, including practicality, reproducibility, simplicity, and a high QY. Nevertheless, it is difficult to distinguish tiny precursors from basic materials.

Liu et al. [41] introduced a new technique for producing CQDs by subjecting resol (a carbon source) and surfactant-modified silica spheres to pyrolysis. The produced CQDs displayed blue fluorescence and had an amorphous structure. The diameters of the CQDs ranged from 1.5 to 2.5 nm, QY achieved was 14.7%. Furthermore, the CQDs exhibited stability throughout a wide pH range, namely pH 5 to 9. Subsequently, further experiments were conducted to create CQDs employing the pyrolysis technique. Pan et al.[42] produced very blue luminescent CQDs by subjecting ethylenediamine-tetraacetic acid (EDTA) salts to pyrolysis. The mean diameter of the synthesized CQDs was 6 nm. The measured QY was determined to be 40.6% [80]. Martindale et al. [43]produced fluorescent CQDs with an average size of 6 nm by subjecting citric acid to pyrolysis at a temperature of 180 °C. QY of these CQDs, evaluated at an excitation wavelength of 360 nm, was determined to be 2.3%.

Rong et al.[44] produced fluorescent N-CQDs by heating citric acid and guanidinium chloride. They did not use any organic solvent, acid, alkali, or further modification and passivation. The resultant N-CQDs had a size of 2.2 nm and a QY of 19.2%. They extensively used N-CQDs for the detection of metal-ion (Fe^{3+}) and in bio-imaging. Recently, the pyrolysis approach was used to synthesize many CQDs, which were subsequently applied in various sectors [45].

2.2.4 .Microwave Irradiation Method

Microwave synthesis is an expedient and economical approach for producing CQDs by the use of microwave heating. Compared to other methods, this methodology is straightforward and convenient due to its shorter synthesis time for CQDs, resulting in an enhanced quantum yield. Zhu et al.[46] first produced fluorescent CQDs by subjecting poly (ethylene glycol) (PEG-200) and saccharide to microwave heating at 500W for a duration of 2-10 min . This approach is characterized by its rapidity, novelty, environmental friendliness, and energy efficiency in synthesizing CQDs. Nevertheless, there are several constraints to consider, including challenges in the separation and purification process, as well as the limited potential uses of CQDs due to their non-uniform particle sizes [47]. Recently, researchers conducted many studies to create CQDs employing microwave irradiation and explore their applications[48-50].

2.2.5 .Template Method

Bourlinos et al.[51] first produced luminescent CQDs by the template approach . The template technique consists of two distinct steps: (i) The production of CQDs by the process of calcination in a suitable template or silicon sphere. (ii) The etching procedure is carried out to remove the supporting materials. The template approach has many positive qualities, including its simplicity, the availability of equipment, its applicability for surface passivation of CQDs,

its ability to avoid particle agglomeration, and its control over the size of CQDs. An unfavorable characteristic of the template approach is the challenge in extracting the CQDs from the template, which may impact the purity, particle size, fluorescence, and quantum yield.

3 .Optical Properties of CQDs

3.1 .Absorbance

Carbon quantum dots typically display two absorption bands in the visible spectrum at approximately 280 nm and 350 nm, accompanied by a large tail in the ultraviolet range. Hu et al. [52] indicated that an absorption band at 280 nm results from a π-π* transition of a C=C bond, whereas the band at 350 nm arises from an n-π* transition of the C=O bond. The absorption characteristics of CQDs can be affected by surface modification or surface passivation. The positions of these absorption bands vary to some degree based on the raw precursor and synthesis methods employed. Doping in CQDs can modify the absorption wavelength[53, 54]**.**

The optical characteristics of CQDs can be tailored through doping or co-doping with heteroatoms, functional groups, and surface passivation [55]. During surface passivation, a thin insulating layer composed of compounds such as thiols, thionyl chloride, spiropyrans, and oligomers (e.g., polyethylene glycol (PEG)) is established on the surface of CQDs. The primary functions of these protective layers are to safeguard CQDs from impurity adherence and to ensure stability. Surface-passivated CQDs have significant optical activity, displaying substantial fluorescence from the visible to the near-infrared spectrum [56]. QYs of CQDs can be improved to 55–60% through surface passivation. The absorbance of CQDs increased at longer wavelengths (350–550 nm) following surface passivation using 4,7,10-trioxa-1,13-tridecanediamine (TTDDA) [57]. The size of particles correlates with the wavelength of absorption. As the dimensions of the CQDs augment, the absorption wavelength correspondingly increases [58].The CQDs are suitable for covalent bonding with functionalizing agents. Various functional groups, including amines, carboxyl, hydroxyl, and carbonyl, were incorporated onto the surface of CQDs using surface functionalization. The functionalized CQDs demonstrated excellent biocompatibility, high stability, remarkable photo reversibility, and reduced toxicity in comparison to undoped CQDs. The effective method to alter the absorption spectra of CQDs is through doping or co-doping with heteroatoms, including boron (B), nitrogen (N), fluorine (F), phosphorus (P), and sulfur (S). The dopant modifies the bandgap, electronic structure, and, therefore, the optical properties of CQDs by changing the π-π* energy level associated with the core-sp2 carbon system [120]. An increase in N-dopant concentration resulted in a gradual elevation of the band gap of the CQDs from 2.2 to 2.7 eV [59]. Conversely, it was discovered that nitrogen doping in carbon quantum dots leads to a decrease in size [60]. The CQDs created novel electronic states, leading to a decrease in the bandgap of CQDs (about 48–57%) [61]. Zuo et al.[62] produced F-doped carbon quantum dots via a hydrothermal technique, demonstrating elevated quantum yields, improved electron transport, and greater photocatalytic performance .

3.2 .Photoluminescence

Photoluminescence (PL) refers to the emission of light from a substance following the absorption of light (photon). Photoluminescence encompasses two categories: fluorescence and phosphorescence. Fluorescent materials emit absorbed light from the lowest singlet excited state (S1) to the singlet ground state (S0). This process is exceedingly rapid and possesses a millisecond duration. The transitions between two electronic states in the fluorescence process are permitted due to their identical spin multiplicity. Conversely, in phosphorescence, the transition transpires from the lowest triplet excited state (T1) to the singlet ground state (S0), signifying a forbidden transition as per the spin selection rule[63].

3.2.1 .Phosphorescence

Phosphorescence in CQDs was initially reported by De et al. by the dispersion of CQDs in a polyvinyl alcohol matrix at room temperature and their excitation with UV light. The peak emission recorded was 500 nm, accompanied by an average lifespan of 380 ns under 325 nm stimulation [64]. Phosphorescence in CQDs occurs when the singlet and triplet states of an aromatic carbonyl group within the CQDs and polyvinyl alcohol matrix are energetically proximate, facilitating spin–orbit coupling and enhancing intersystem crossover (ISC). Lu et al.[65] created ultra-long phosphorescent carbon quantum dots (P-CQDs) using microwave synthesis. P-CQDs exhibited yellow-green phosphorescence (525 nm) for a duration of up to 9 seconds when activated at 354 nm. They determined that as the pH rises, the phosphorescence intensity of P-CQDs progressively diminishes. Protonation disrupts hydrogen bonds and compromises the phosphorescent sources. The introduction of tetracyclines (TCs) resulted in the quenching of P-CQDs' phosphorescence. P-CQDs were utilized for biological and chemical sensing as well as time-resolved imaging.

3.2.2 .Electrochemiluminescence

CQDs can generate photons in the visible spectrum when subjected to electrical excitation, which is crucial for investigating their electrochemiluminescence (ECL) characteristics. The substantial presence of sp2 carbon in carbon dots facilitates improved electron transport, leading to a stable ECL [66].

3.2.3 .Chemiluminescence

Chemiluminescence (CL) generates light through a chemical reaction. Under suitable conditions in redox reactions, carbon dots can produce chemiluminescence in aqueous solvents, where unstable compounds arise from intermediate radicals throughout the chemiluminescence process. CQDs can produce CL either through excitation following direct oxidation or via the modulation of their luminescence[67].

3.2.4 .Fluorescence

The fluorescence characteristics of CQDs have garnered significant interest from researchers due to their numerous sensing and analytical applications. Various methods have been documented to elucidate the origins of fluorescence in CQDs[68, 69]. Among them, the following two have been identified as more significant. The fluorescence process originates from transitions in band gaps associated with π-conjugated domains (sp2-hybridized), akin to aromatic compounds that utilize specific energy band gaps for absorption and emission. The secondary cause of fluorescence pertains to surface defects, the quantum size effect, carbon core states, surface passivation or functionalization effects, and other emissive traps present on the surface of CQDs[70].

The primary cause of surface defects in CQDs is the asymmetrical distribution of sp2- and sp3-hybridized carbon atoms, along with the presence of heteroatoms such as boron, nitrogen, phosphorus, and sulfur [71]. The autonomous incorporation of this surface defect into the solid host generates an environment akin to that of aromatic molecules. These compounds can absorb UV light and exhibit diverse color emissions [72].CQDs exhibit two forms of emission: excitation-dependent emission (tunable emission) and excitation-independent emission. The tunable emission arises from the availability of diverse emission sites on the surface of CQDs, coupled with particle size dispersion; hence, most CQDs demonstrate tunable emissions [73]. The excitation-independent emission results from the highly organized graphitic structure of CQDs .CQDs demonstrate broad and persistent excitation spectra, characterized by strong photostability and consistent fluorescence, unlike conventional organic dyes[74] .

3.3 .Biological Performance

Typically, low doses of CQD solutions exhibit minimal toxicity to human cells and may, in certain instances, even enhance cellular proliferation. Nonetheless, the cytotoxicity of CQDs markedly escalates with increased concentration to a specific threshold, hence exhibiting superior biocompatibility and reduced cytotoxicity in comparison to conventional

semiconductor quantum dots. They demonstrate advantageous water solubility and stability, making them appropriate for incorporation with biomolecules or medicines to enhance bioimaging, drug delivery, and photodiagnostics. The fluorescence emission capability of carbon quantum dots makes them useful as fluorescent probes for detection and analytical applications. Furthermore, the exceptional biocompatibility and low toxicity of carbon dots promote their incorporation into cellular structures[75].Thus, carbon dots with diverse properties can be efficiently utilized for imaging within organisms and for medication delivery.

Tungare et al. [76] produced and studied CQDs derived from palm fruits by microwave-assisted pyrolysis. The resultant CQDs were quasi-spherical and spatially homogeneous. Biocompatibility assessments were performed utilizing various model systems. The findings indicated that CQDs were non-cytotoxic in the WRL-68 cell line, although shown minimal toxicity in HT1080 cells. This indicated a possibility for synergistic eradication of cancer cells. The phytotoxicity evaluation of plants from four distinct seedlings indicated that the CQDs were non-toxic. Furthermore, these CQDs did not impede microbial proliferation and did not influence the development of zebrafish embryos. Consequently, these CQDs possess significant prospective applications in biological domains, including biomolecular detection, medication release regulation, as well as serving as drug carriers and fluorescent tracers.

3.4 .Chemically Inertness

The chemical inertness of CQDs is defined by their surface stability and diminished reactivity with other chemicals. The property is predominantly determined by the surface functional groups of the carbon quantum dots. Yang et al. [77] emphasized the remarkable chemical durability of CQDs, allowing them to maintain enhanced fluorescence intensity and quantum yield even in harsh settings, including high concentrations, rising temperatures, and exposure to strong acids and bases. The exceptional stability and inertness enhance the strong performance of CQDs.

3.5 .Adsorption Properties

CQDs possess remarkable adsorption ability due to their high specific surface area, active surface, abundant functional groups, and porous architecture [78]. They demonstrate the ability to adsorb organic molecules, metal ions, toxic compounds, and gasses.The adsorption properties of carbon quantum dots are applicable in several areas, including the removal of environmental pollutants, drug delivery, and photocatalysis. These remarkable qualities render carbon quantum dots proficient in adsorbing organic contaminants in water, such as colors [79], antibiotics [80], and insecticides [81]. Wang et al. [82] assert that the adsorption efficacy of CQDs is affected by multiple aspects, including their synthesis process, structural characteristics, composition, surface modifications, and the pH, temperature, ionic strength, and content of organic matter in water. The adsorption mechanism primarily involves electrostatic interactions, hydrogen bonding, π-π stacking, and van der Waals forces. Unique organic contaminants may display differing predominant influences.

4 .Characterization Techniques for CQDs

Various characterization techniques are currently being used to study the morphology (size, shape, and structure), topography, elemental composition, crystallographic information, size distribution, and granular orientation of different types of CQDs prepared using various synthetic methods. The main techniques used include microscopy, spectrometry, spectroscopy, and diffraction.

4.1 .Characterization of CQDs by Mass Spectrometry

The chemical structures of desirable nanosized CQDs can be clarified by the use of mass spectroscopy, an excellent method for characterizing CQDs [83]. Techniques including matrix aided laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) and electrospray ionization quadrupole time-of-flight tandem mass spectrometry (ESIQ-TOF-MS/MS) are used in this procedure.

4.1.1 .Matrix-Assisted Laser Desorption/Ionization Time-Of-Flight Mass Spectrometry

A soft ionization technique called MALDI-TOF-MS has been used to describe the structure of CQDs. This approach uses the difference in flight periods, when ions of the same energy level are directed toward the detector, to calculate the mass of the ions. Mass accuracy using MALDI-TOF MS is as excellent as 0.1[83-85] .

Hu et al.[86] created a method to categorize CQDs based on their fragmentation using this methodology. Figure 2, a typical example of MALDI-TOF MS analysis, describes the structural elucidation of CQDs produced by microwave-assisted pyrolysis of 1,2-ethylenediamine and citric acid [86]. The CQDs in this investigation were first separated using reverse phase high performance liquid chromatography (RP-HPLC), after which the fractions were collected and subsequently characterized using MALDI-TOF MS in a positive ionization mode under a pulsed N2 laser. Because of the amine/amide and carboxylic acid moieties affixed to their surface, each percentage of CQDs was able to display the unique fragmentation pattern [86]. While this technique can identify the chemical functions of CQDs, it is not as sensitive to higher masses and cannot separate the larger ions with greater mass range[83] .
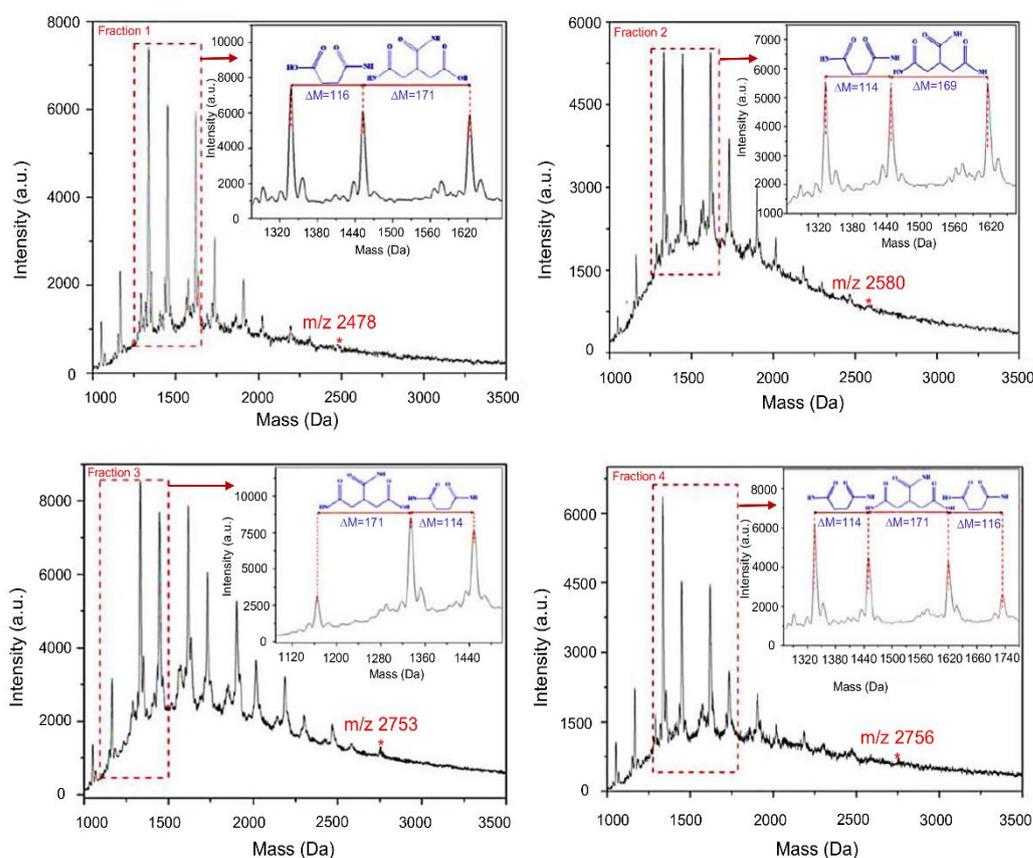

Fig.2 Different MS spectra from MALDI-TOF MS analysis of different CD fractions are graphically shown (Reproduced from Hu et al.[86]).

4.1.2 .Electrospray Ionization Quadrupole Time-Of-Flight Tandem Mass Spectrometry

Both the soft ionization approach and sensitive MS detection are used in ESIQ-TOF-MS/MS [83]. Hu et al.[85] employed ESIQ-TOF-MS/MS in conjunction with ultraperformance liquid chromatography (UPLC) to characterize the CQDs .The chemical formulas for specific CQDs were obtained by concurrently capturing the MS/MS and MS spectra for CD characterisation, as shown in Figure 3. According to these investigations, CQDs exhibit supramolecular clusters in which the monomer units are associated by noncovalent contact [84, 85] .
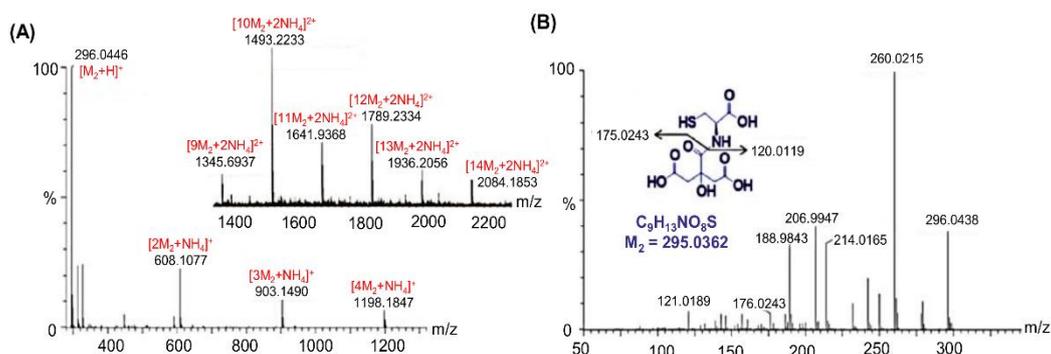
Fig.3 Depiction of (A) mass spectrometry spectrum. MS/MS spectrum derived from ESI-TOF-MS investigation of carbon dots. Inset: Mass spectrometry spectra of the carbon dots in elevated m/z ranges (Reproduced with permission from Hu et al.[87]).

4.2 .Characterization of CQDs by Spectroscopy

CQDs have been characterized using a range of spectroscopic techniques, including ultraviolet-visible (UV-Vis), infrared (IR), photoluminescence (PL), dynamic light scattering (DLS), Raman spectroscopy (RS), energy dispersive X-ray (EDX), nuclear magnetic resonance (NMR), and X-ray photoelectron spectroscopy.

4.2.1 .Photoluminescence and Ultraviolet-Visible Spectroscopy

PL and UV-Vis spectroscopies are widely used techniques for investigating the optical properties of CQDs. Moreover, these two spectroscopies may specifically be used to calculate the quantum yield (QY) of CQDs[88-90] .Typically, all types of CQDs exhibit their activities within the UV-Vis area of the electromagnetic spectrum. In addition, the fluorescence of CQDs exhibits emission that is dependent on the excitation wavelength (λex). Photoluminescence (PL) spectroscopy is frequently employed to measure the photoluminescent lifespan of CQDs[88, 89].

4.2.2 .Infrared Spectroscopy

Infrared spectroscopy (IR) is a widely used method for analyzing the chemical properties of CQDs . Infrared spectroscopy (IR) may be used to assess the presence of carbonyl (C=O) and hydroxyl (–OH) groups on the surface of CQDs. Additionally, it can identify the heteroatoms that have been doped onto their surface[91, 92] . The IR analysis has shown significant illustrations of the presence of boronic acid (B–N and B–O), phosphates (P=O and P–OR), organosiloxane (Si–OSi/Si–O–C), alkyl sulfide (C–S), and amide/amine (–CN/NH$_2$) functionalities on the surface of the CQDs. This confirms the incorporation of boron (B), phosphorus (P), silicon (Si), sulfur (S), and nitrogen (N), respectively [83]. IR spectroscopy has several benefits including convenient sample preparation, fast analysis, simplicity, and cost-effectiveness. However, infrared (IR) technology is incapable of extracting specific information on the presence of metal heteroatoms such as nickel (Ni), magnesium (Mg), and aluminum (Al) in CQDs [83]. Furthermore, Fourier transform infrared (FTIR) spectroscopy may be employed to analyze CQDs that possess hydroxyl, carboxyl, carboxylic acid, ether, or epoxy functionalities. FTIR is a highly reliable technique for evaluating functional groups that include a significant amount of oxygen.

4.2.3 .Raman Spectroscopy

Raman spectroscopy is a widely employed technique for assessing the carbon state of carbon dot materials.It is a non-invasive and non-destructive spectroscopic method[93].Raman spectroscopy of CQDs often displays two significant first-order bands: the G band and the D band. The initial phenomenon pertains to the oscillation of sp2 carbon atoms in a two-dimensional hexagonal configuration, whereas the subsequent phenomenon relates to the vibrations of carbon atoms with unpaired bonds in the outermost layer of disordered glassy carbon or graphite. The graphitization or disorder degree of CQDs, indicative of sample purity,

is assessed by the intensity ratio (D/G) of these two bands [94]. Figure 4 illustrates the Raman spectra of carbon dots, indicating the existence of the G band at 1578 cm^{-1} and the D band at 1331 cm^{-1}, respectively [95]. The D/G ratio was calculated to be 0.59, signifying the existence of a nanocrystalline graphite structure in carbon dots. The D′ band at 2654 cm^{-1} signifies the presence of carbon atoms exhibiting sp2 hybridization [95]. Acquiring high-resolution Raman spectra can be difficult in certain circumstances due to the pronounced fluorescence of carbon dots, which hinders the generation of a clear Raman signal .
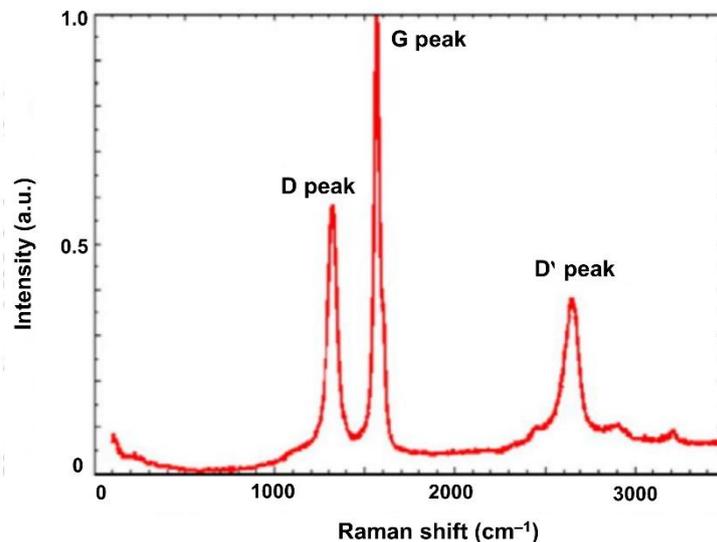

Fig.4 An illustration of the Raman spectra of carbon dots. (Reproduced with permission from Mewada et al.[95]).

4.2.4 .Nuclear Magnetic Resonance Spectroscopy

NMR spectroscopy is employed to provide additional and essential structural information for CQDs. This method enables the detection of chemical bond forms, elemental composition, and the existence of functional groups on the surface of CQDs. Furthermore, NMR can identify the chemical changes that occurred during carbonization due to the surface modifications. Furthermore, the application of NMR for the evaluation of CQDs is quite uncomplicated owing to its non-invasive characteristics. NMR possesses notable disadvantages, such as reduced sensitivity, extended analysis duration, and elevated costs, relative to mass spectrometry techniques. Figure 5 illustrates the representative NMR spectra employed to characterize CQDs.
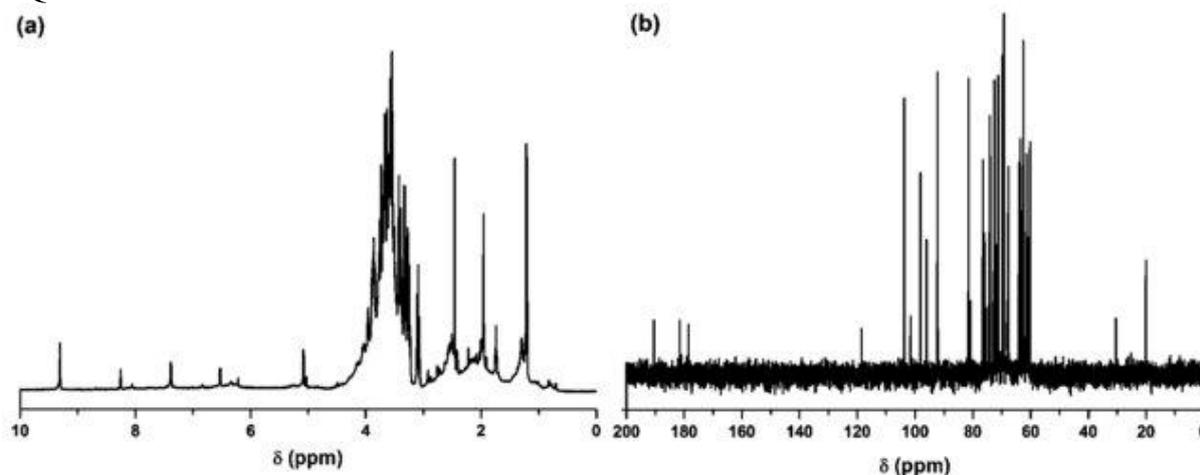

Fig.5 (a) 1 H-NMR and (b) 13 C-NMR spectra of the carbon dots **(**Reproduced with permission from Bibekananda et al.[96]**)** .

4.2.5 .Dynamic Light Scattering, and Zeta Potential Measurements

The DLS approach, when combined with liquid phase analysis using certain detection equipment, is used to determine the hydrodynamic particle size for characterizing CQDs. This approach allows for the evaluation of CD radii by measuring the diffusion rate of CQDs in liquified liquid. Nevertheless, the drawback of utilizing this approach lies in its lack of dependability and precision, as the dynamic light scattering (DLS) technique only provides data on the size distribution of colloidal particles based on the produced photon complementary function[97, 98] . In addition, zeta-potential measurements may be used to assess both the surface charge and particle size of CQDs. These measurements are widely used to characterize the chemical functionalization on the surface of CQDs [99]. The zeta-potential indicates the level of repulsion between particles that have the same charge and are close to one other in a dispersion, thereby controlling the stability of CQDs. Furthermore, this approach offers details on the attributes of CQDs, including the features of double layers with diverse hydrophilic functional groups (hydroxyl, carboxyl, and carbonyl)[99, 100] .

4.2.6 .X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is employed to analyze the electronic configuration of the elements found on the surface of CQDs, determine their elemental makeup, and examine other surface properties. X-ray XPS involves directing a beam of X-rays at the specimen of CQDs. This is followed by irradiating the sample and simultaneously measuring the kinetic energy and quantity of electrons[83, 101] . Figure 6 illustrates the optimal XPS spectra for the characterisation of CQDs [88]. However, XPS is incapable of identifying individual nanoparticles because it lacks spatial resolution [83].
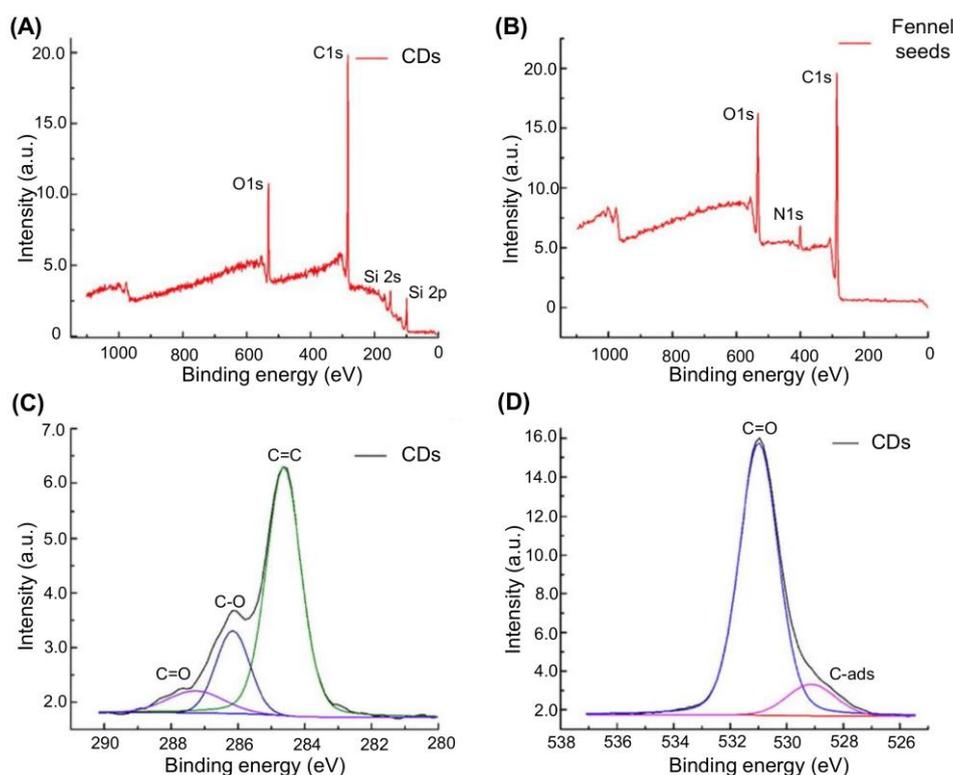

Fig.6 XPS spectra of: (A) CQDs revealing O1s and C1s peaks. (B) Fennel seeds with C, N, and O composition. (C) C1s. (D) O1s (Reproduced from Dager et al.[88]**).**

4.3 .Characterization of CQDs by Microscopy

The morphology of CQDs is often characterized using several microscopic approaches. By utilizing these microscopic techniques, it is possible to accurately determine the size of particles by directly measuring each individual nanoparticle. CQDs are primarily distinguished by

microscopic techniques such as atomic force microscopy (AFM), transmission electron microscopy (TEM), and scanning electron microscopy (SEM).

4.3.1 .Atomic Force Microscopy (AFM)

AFM is an advanced technique that uses a high-resolution scanning probe microscope to acquire a detailed topographical image of a sample surface. This image is generated by analyzing the interactions between a sharp tip and the surface of the sample. An AFM typically consists of a cantilever equipped with a tiny tip (probe) at its free end, a laser, a 4-quadrant photodiode, and a scanner. AFM enables the analysis of CQDs by taking high-resolution surface images of their dimensions at sub-nanometer scales. AFM provides both two-dimensional (2D) and three-dimensional (3D) information from the pictures of CQDs, distinguishing it from other microscopies. The diameters of CQDs may be determined by randomly computing the heights of particles on 2D photos, whereas 3D images reveal the surface morphology of CQDs[83, 102, 103] . Figure 7a and 7b depict the topographical AFM pictures of CQDs in 2D and 3D, respectively[104].
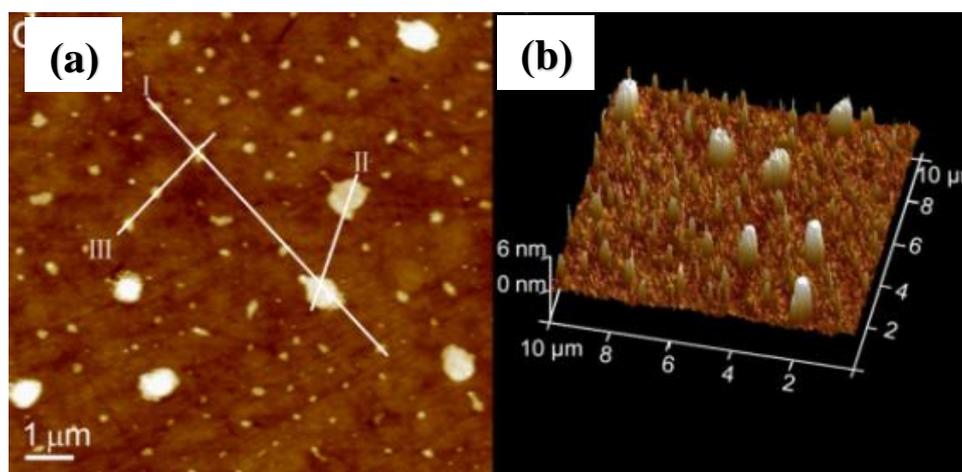

Fig. 7 Microscopic image to characterize CQDs (a) 2D AFM image, (b) 3D AFM image (Reproduced from Huang et al. [104]**).**

4.3.2 .Transmission Electron Microscopy(TEM)

TEM is able to obtain CD pictures and chemical data at a spatial resolution comparable to atomic dimensions. When the electron beam in a TEM meets with a sample of CQDs, it transmits incoming light through a thin foil specimen and changes into elastically or inelastically dispersed electrons. The objective lens, CD specimen, and image plane distance ratio is what is referred to as the lens's magnification. The TEM uses powerful electrons to produce precise particle size of both bright field and dark field pictures as well as information about the shape, composition, and crystallographic characteristics of CQDs[86]. High resolution transmission electron microscopy (HRTEM) is widely used nowadays to investigate the surface and lattice defects of CQDs. Both transmitted and dispersed beams are used by HRTEM to create an interference picture [83]. Figure 8a,b respectively, shows examples of TEM and HRTEM images of CQDs [105].
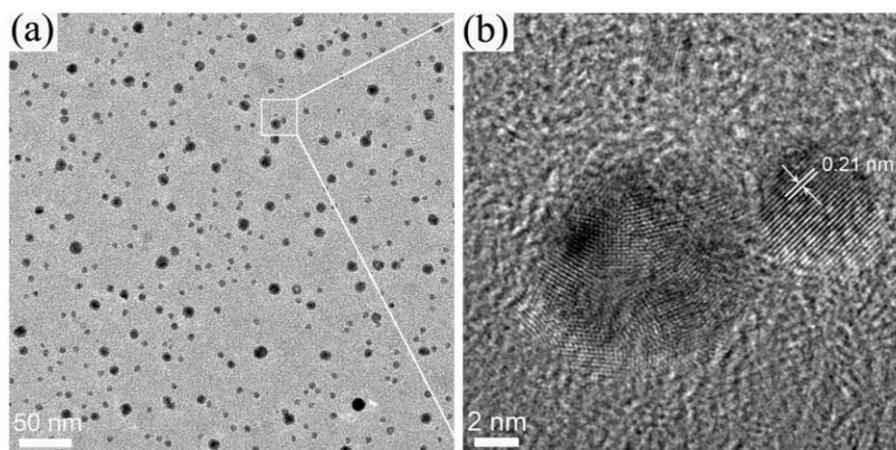
Fig.8 TEM image (a) , (b) HRTEM image (Reproduced from Chen et al.[105]).

4.3.3 .Scanning Electron Microscopy

SEM is able to get spatially resolved images of CQDs for their characterisation. When a CD sample is subjected to a high-energy electron beam in a scanning electron microscope (SEM), the resulting charge buildup creates an image that may be used to extract information on the CQDs' morphology, topography, chemical composition, granular orientation, crystallographic details, etc. Figure 9 shows an example of a SEM picture of CQDs. To determine if CD aggregates are present or absent and to ensure that the CD dispersion is uniform, SEM and TEM can both be used[106]. The TEM has a better resolution power than the SEM. One further drawback of employing SEM is its inability to image CQDs on a big scale. In situations when the measurement exceeds the SEM resolution, TEM may thus be a more advantageous option than SEM [83].
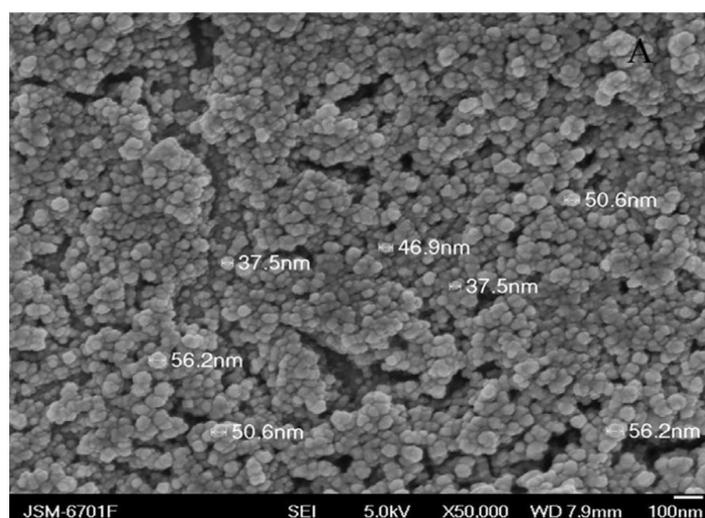

Fig. 9 Image SEM (Reproduced from et al.[106]).

4.4 .Characterization of CQDs by Diffraction Technique

The characterization of CQDs may be accomplished using the X-ray diffraction (XRD) technique. This method allows for the rapid determination of the CQDs' crystalline structure, phase purity, and particle size, based on their diffraction pattern. When X-rays interact with the crystalline structures of CQDs, they undergo diffraction, detection, processing, and computation, resulting in the determination of the CQDs' average structure. It is important to highlight that XRD is not effective in characterizing amorphous CQDs[107, 108] .Figure 10 illustrates a typical example of using XRD to characterize CQDs.
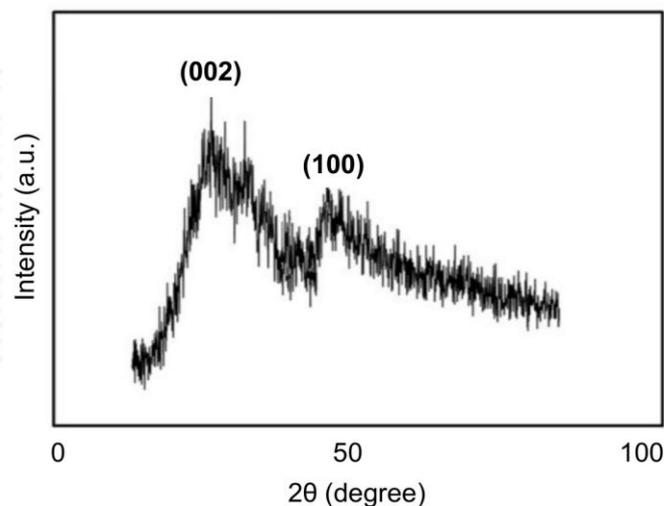
Fig.10 Illustration of a CD XRD pattern (Reproduced from Kazemifard et al. [109]**).**

6 .Carbon Quantum Dot Applications

Carbon quantum dots are a type of nanomaterial that is becoming increasingly popular in many industries due to their optical, electrical, thermal and biocompatible properties. Figure 11 shows the many areas in which carbon quantum dots can be used.
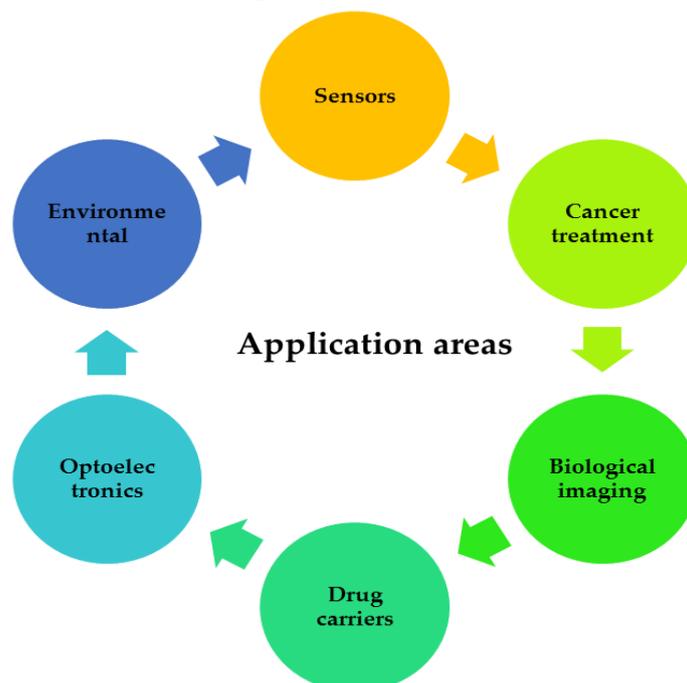

Fig. 11 Carbon quantum dot applications.

6.1 .Environmental Field

CQDs are frequently used in the detection and removal of environmental pollutants because of their stable optical properties, wide range of excitation, capacity to alter emission wavelength, strong chemical stability, high solubility in water, and ease of surface modification. Environmental pollution control and management have long been a significant global concern. Global pollution has escalated to a disastrous extent in recent years. Efficient regulation and supervision of environmental contamination are of utmost importance. CQDs, due to their distinctive fluorescence characteristics, can be employed as exceptionally effective fluorescent probes for the rapid and precise identification of metal ions in the surrounding environment. Zhou et al. [110]produced water-soluble fluorescent CQDs by subjecting EDTA-2Na to high-

temperature pyrolysis. The researchers noted that the CQDs had a strong preference for Hg^{2+} and that cysteine was able to reduce the impact of Hg^{2+} on the fluorescence intensity of the CQDs.

Arumugam et al. [111]produced CQDs by utilizing broccoli as a precursor in a one-step hydrothermal process. The photoluminescent properties of the CQDs were utilized to detect the presence of Ag^+ ions. The results demonstrated a detection limit of 0.5 μmol/L for Ag^+ ions, with a strong linear correlation between the intensity of photoluminescence and the concentration of Ag^+ ions. In addition, the sensor demonstrated selectivity by effectively eliminating interference from other heavy metal ions, such as Cr^{3+} and Mn^{2+}. Liu et al. [112] synthesized CGCS-CQDs by a single-step hydrothermal process utilizing grass carp scales and employed them for the detection of Hg^{2+}. The CGCS-CQDs demonstrated a detection limit of 0.014 micromoles per liter. The detection limit was frequently tested by the same experiments, consistently proving its dependability. Pandey et al. [113] utilized a hydrothermal technique to produce CQDs from curry leaves. These CQDs were then applied for the purpose of detecting Cd^{2+}. The investigation showed that the CQDs had outstanding selectivity, with a detection limit of 0.29 nmol/L and a detection range of 0.01–8.00 μmol/L.

6.2 .Bioimaging

Bioimaging is a technique that allows the real-time visualization of biological processes without causing harm or damage, employing specialized tools and sensors. Fluorescence imaging has become a powerful method for clinical diagnosis due to its simplicity, affordability, high sensitivity, noninvasive nature, and capability for long-term monitoring [114]. Fluorescent materials such as organic dyes, semiconductor quantum dots, and up-conversion nanoparticles are used for bioimaging. However, these materials are unsuitable for application in the biomedical sector because they have a high level of toxicity to cells, are not stable under light, and do not have good compatibility with living organisms [115]. Carbon quantum dots possess excellent photostability, favorable biocompatibility, straightforward synthesis methods, adaptable design options, the capacity to emit light in several colors, crimson or near-infrared emission, and luminescence that may be triggered by two or more photons. These characteristics make carbon quantum dots a promising fluorescent probe for bioimaging both in laboratory settings and inside living organisms[116].

Huang et al. [117]synthesized CQDs using a one-pot hydrothermal method and a by-product of the biorefining process (degradation product of biomass autohydrolysis) as a carbon source. They then analyzed the CQDs' morphology, structure, and optical properties using different characterization techniques. The researchers discovered that the CQDs had a size distribution ranging from 2.0 to 6.0 nm, a significant proportion of sp2 and sp3 carbon bonds, and emitted blue-green fluorescence with a quantum yield of approximately 13%. Furthermore, the researchers also discovered that CQDs exhibit excellent photostability and temperature stability, and are not susceptible to photobleaching and fluorescence bursts.

This characteristic renders them very appropriate for prolonged optical monitoring. Fluorescence imaging was conducted on the mice at various time intervals. The fluorescent signals emitted by the mice were subjected to quantitative analysis. It was observed that the distribution of CQDs in the mice was mostly localized in the liver and spleen, as seen in Figure 12a. This distribution pattern closely resembled the in vivo behavior of other nanomaterials. The results demonstrated a progressive increase in the fluorescence signals at the tumor locations over time (see Figure 12b), suggesting that the CQDs exhibited effective tumor targeting capabilities. The toxicity response of CQDs in mice was assessed using blood biochemical analysis and histological inspection. The results indicated that CQDs did not induce acute toxicity or cause liver and kidney damage in animals, suggesting that CQDs exhibit favorable biocompatibility.
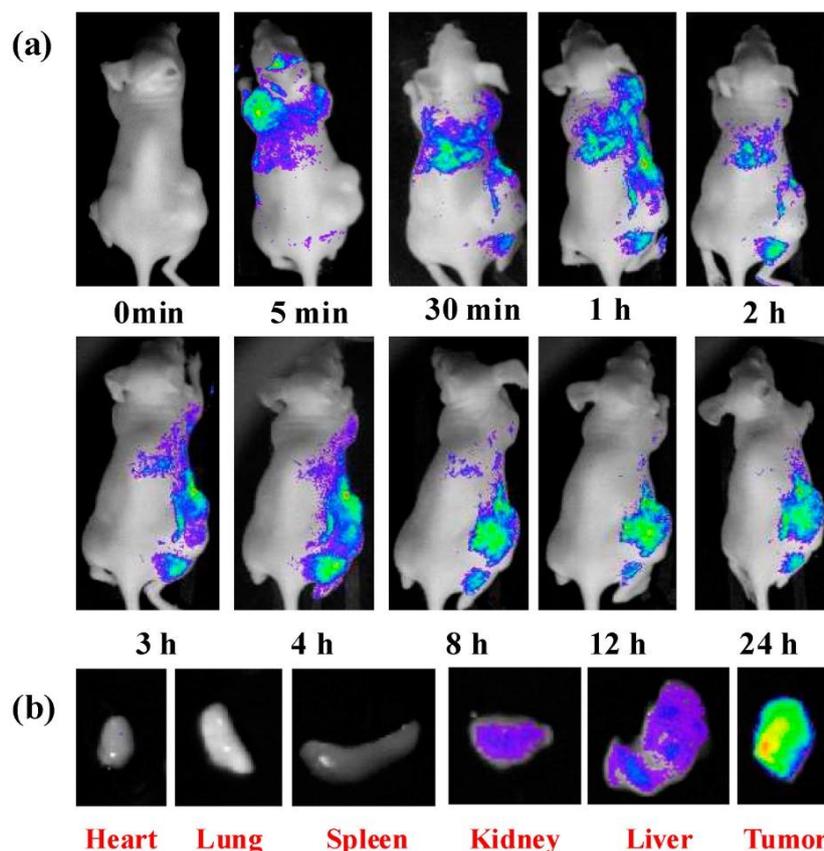
Fig. 12 (a) Fluorescence imaging in vivo of nude mice following intravenous injection of CQD-WS solution; (b) Fluorescence pictures indicative of a mouse's dissected organs following a 24-h intravenous infusion of CQD-WS solution (Reproduced with permission Huang et al.[117]).

6.3 .Optoelectronics

Mirtchev et al. [118] produced CQDs that include a high concentration of hydroxyl, carboxyl, and sulfonate groups. They achieved this by oxidizing γ-butyrolactone by sulfuric acid dehydration. The researchers utilized CQDs as a sensitizer for TiO_2, leading to a short-circuit current of 0.53 $mA.cm^{-2}$, a fill factor of 0.64, an open-circuit voltage of 0.38 V, and a total power conversion efficiency of 0.13%. The overall power conversion efficiency of unsensitized TiO_2 nanocrystals was about 0.03%. An initial inquiry into the application of carbon quantum dots fixed on nanocrystalline titanium dioxide as sensitizers for titanium dioxide solar cells showcased their promising capabilities. Zhang et al.[119] constructed cationic energy cells by utilizing NCQDs as sensitizers. Under sunshine irradiation (AM 1.5), the open-circuit voltage and fill factor values were 0.46 V and 43%, respectively. The linked gadget obtained an energy conversion efficiency of 0.13%. Xiong et al. [120] employed an electrochemical stripping technique aided by an ionic solution containing 1-butyl-3-methylimidazolium hexafluorophosphate and 1-butyl-3-methylimidazolium tetrafluoroborate to synthesize two variants of CQDs. Subsequently, the CQD samples were utilized in the fabrication of dye-sensitized solar cells, resulting in energy conversion efficiencies of 2.71% and 2.41% for each sample, respectively.

Shen et al. [121] produced boron-doped carbon dots (B-CQDs) by a hydrothermal process utilizing boric acid and ethylenediamine as precursor materials. This approach resulted in a quantum yield of 54%. The B-CQDs-LEDs they created had a luminosity of around 250 $cd.cm^{-2}$ when operated at a voltage of 3.2 V. This level of brightness could be sustained for almost 24 h. Yang et al. [122] synthesized several types of N-CQDs by utilizing chitosan as a carbon and nitrogen source through the hydrothermal technique at varying reaction durations (as seen in

Figure 13a). Subsequently, the researchers assessed the efficacy of the N-CQDs in DSSCs by conducting electrochemical and photoelectric conversion efficiency examinations. The study revealed that the N-CQDs have the ability to function as a co-sensitizer, resulting in a synergistic enhancement of the open-circuit voltage (Voc), short-circuit current density (Jsc), fill factor (FF), and photoelectric conversion efficiency (PCE) of DSSCs when utilizing N719 dye. Figure 13b,c shows that when exposed to typical sunlight (AM 1.5) irradiation, one of the devices that were produced attained a power conversion efficiency (PCE) of up to 9.15%. The efficiency of the device with N-CQDs is markedly higher compared to the regulated device, which has an efficiency of 8.5%. Figure 13d depicts the internal arrangement of the co-sensitized solar cell.

Han et al. [123]synthesized CQDs with a high level of luminescence, achieving a quantum yield of up to 84.8%. This was accomplished by the utilization of a hydrothermal technique. The carbon source utilized was citric acid, while the nitrogen source employed was ethylenediamine. Additionally, a small amount of ammonia was added to attain favorable internal structure and superior nitrogen passivation capabilities. In order to achieve a high-yield solution of CQDs, an aqueous solution of CQDs was combined with a 5 wt.% aqueous solution of polyvinyl alcohol (PVA). The solution was applied onto silicon nanowire solar cells using a spin-coating technique and then subjected to a temperature of 80 °C for a duration of 20 min to create an EDS layer. The layer's thickness was modified by varying the number of spin coats. The inclusion of the EDS layer led to a significant improvement in JSC, resulting in a rise in PCE from 10.85% to 10.96%. The enhanced mechanism was ascribed to the conflicting impacts of surface reperformance deterioration and redistribution of light absorption**.**
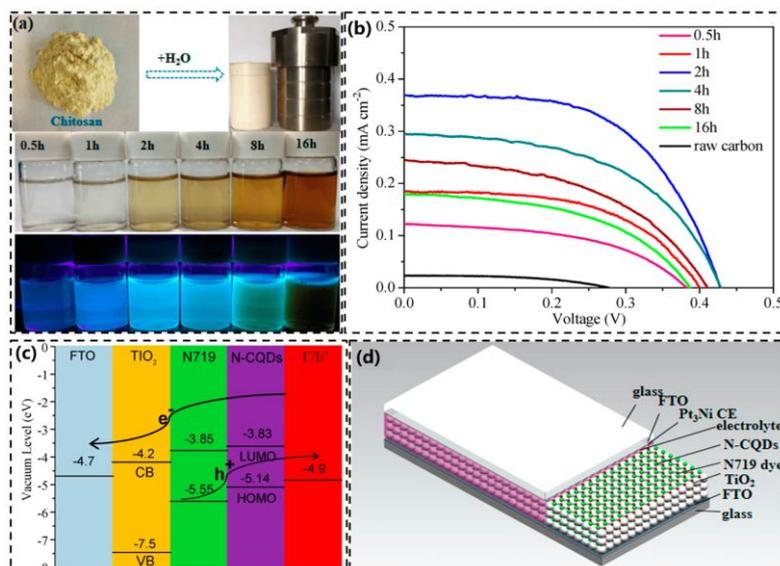

Fig.13 (a) Images of nitro-doped carbon quantum dots (N-CQDs) in aqueous solutions made during UV irradiation with varying heating durations, as well as the conversion of chitosan powder into CQDs using a hydrothermal technique. (b) Under simulated sunshine (AM1.5, 100 mW.cm^{-2}), the photocurrent density-voltage (J-V) characteristic curve of an N-CQDs sensitized solar cell is displayed. (c) N-CQD energy levels at various heating periods. (d) The co-sensitized solar cells' schematic diagram. (Reproduced Yang et al.[122]).

Ding et al. [124] introduced a very efficient technique for manufacturing white light-emitting diodes (WLEDs) that have a high color rendering index (CRI) and can be adjusted to different correlated color temperatures (CCT). The researchers produced CQDs with varying emission colors by conducting a one-pot solvothermal reaction of phthalic acid and phthalimide, resulting in long-wavelength CQDs. CQDs were designated as G-CQDs , Y-CQDs , and O-CQDs . Subsequently, the processes behind the luminescence of these three forms of

carbon quantum dots were investigated. The luminescence of the G-CQDs and Y-CQDs was mostly attributed to the quantum size effect, whereas the photoluminescence of the O-CQDs originated predominantly from surface defect states resulting from surface oxidation. The preparation of solid-state red-green-blue CQD films involved the utilization of trifunctional blue-emitting CQDs, which served as phosphor, dispersion, and curing agent. Subsequently, these films were utilized to create UV-pumped WLEDs that demonstrate excellent color stability, a high Color Rendering Index (CRI) ranging from 83 to 88, and the capacity to adjust the Correlated Color Temperature (CCT) within the range of 3466 to 7368 K. This work facilitated the advancement of cost-effective, eco-friendly, and high-performing CQD phosphors for WLEDs.

6.4 .Cancer Treatment

Currently, cancer ranks as the second most common cause of death globally, contributing to millions of fatalities each year [125]. Prompt detection and good treatment are essential for the remediation of cancer. The conventional medical interventions for treating the ailment are limited in their scope of effectiveness and have noticeable harmful effects on the entire body. Nanomaterials with advanced properties are assisting cancer biologists in addressing several challenges such as hypoxia, the tumor microenvironment, low stability, poor penetration, lack of target specificity, quick medication clearance, and improving treatment effectiveness [126]. In recent decades, researchers from several scientific disciplines, including biomedicine, have shown great interest in carbon nanomaterials such as fullerenes, carbon nanotubes, and carbon dots. This is due to their exceptional physical and chemical characteristics, as well as their ability to interact well with biological systems. Carbon nanoparticles have become a new method for delivering anticancer medications because of their durability and capacity to be modified [127].

6.4.1 .Photodynamic Therapy

Reactive oxygen radicals (ROS) are produced at the tumor site by photodynamic treatment (PDT), which uses certain light wavelengths to activate photosensitizers and kill tumor cells. Natural or artificial organic substances, known as photosensitizers, are usually injected intravenously or locally into the tumor tissue. One benefit of photodynamic treatment is its ability to target tumors specifically and provide long-lasting inhibitory effects. Hypoxic cancers cannot be treated with photodynamic therapy due to its oxygen-dependent nature. Photosensitization-related harm to the skin and eyes may also result from photosensitizers. Moreover, photosensitizers' stability and targeting capacity require enhancement [128]. Chen et al. [129] used aldehyde-containing carbon quantum dots with p-phenylenediamine and BODIPY as model monomers to create nanoscale COFs (covalent organic frameworks), designated CCOF-1 and CCOF-2. The resultant CCOF-1 and CCOF-2@PEG were stable and evenly distributed in an aqueous solution following modification with polyethylene glycol. CCOF-2@PEG also shown strong reactive oxygen species generation, excellent physiological stability, and great biocompatibility, which made it a suitable photodynamic therapy (PDT) medication for the treatment of tumors.

6.4.2 .Photothermal Therapy

Photothermal treatment (PTT) employs certain light wavelengths to activate a photothermal agent, causing the production of high temperatures at the tumor location, thus eliminating tumor cells. The photothermal agents can be in the form of metal nanoparticles, carbon nanomaterials, or organic dyes, among other forms. These agents can be delivered either intravenously or locally into the tumor tissue. Photothermal treatment has the benefit of swiftly and effectively eliminating malignancies with minimum harm to healthy tissues [128]. Photothermal therapy is constrained by several limitations. These include the restricted ability of light to penetrate deeply, making it difficult to treat tumors located deep within the body. Additionally, the uneven distribution of photothermal agents can result in the presence of residual tumor cells. Furthermore, there is a need for further assessment of the safety and clearance of these

photothermal agents. Carbon dots are appealing photothermal agents because of their abundance of π electrons and their resemblance to the free electrons found in metallic nanomaterials. Zheng et al. [130] used cyanine dye (CyOH) and polyethylene glycol (PEG800) as starting ingredients to create CyCQDs for near-infrared (NIR) imaging and photothermal treatment. The CyCQDs had a peak emission at 820 nm, reaching their highest intensity. Additionally, they demonstrated a high efficiency in converting light into heat (photothermal conversion efficiency) with a value of 38.7%. Furthermore, they showed exceptional capability in specifically targeting tumors.

Bao et al. [131] produced carbon quantum dots (NIR CQDs) that exhibit near-infrared fluorescence. They used a hydrothermal technique with sulfur- and nitrogen-containing organics as a carbon source. The near-infrared (NIR) CQDs were employed for PTT and optical imaging in a mouse model. The study revealed that the near-infrared carbon dots (NIR CQDs) have an impressive photothermal conversion efficiency of 59%. Furthermore, they can be quickly heated when exposed to 808 nm laser irradiation, resulting in the effective eradication of tumor cells. Moreover, NIR CQDs had exceptional optical characteristics that allowed for in vivo visibility using fluorescence and photoacoustic imaging, which facilitated the location and monitoring of tumors. Moreover, NIR CQDs may be administered intravenously to mice and selectively accumulate in tumor tissues via a passive targeting mechanism, therefore augmenting the efficacy of PTT. Unlike other types of nanomaterials, these nanomaterials have the ability to be eliminated from the body through the kidneys, thereby preventing any build-up or accumulation in the body. The scientists found that the effective conversion of light into heat, together with the ability to produce high-quality images using light and sound, the ability to be excreted by the kidneys, and the ability to target specific areas using near-infrared carbon dots, make them very promising for use in clinical settings and as a therapeutic agent in living organisms.

6.5 .Drug Delivery

CQDs offer significant potential as nanocarriers in advanced drug delivery systems due to their unique properties, such as biocompatibility, tunable surface chemistry, and photoluminescence[132]. To optimize their use in targeted drug delivery, CQDs should be functionalized with biomolecules or polymers, such as polyethylene glycol (PEG) or cyclodextrins, to enhance water solubility and enable precise targeting of diseased cells, such as cancerous tissues, while minimizing impact on healthy cells. For instance, CQDs loaded with anticancer drugs like doxorubicin have demonstrated superior efficacy, reducing cancer cell viability significantly compared to free drugs, according to research by Kong et al. [133], MCF-7 breast cancer cells may be effectively treated for human breast cancer by administering doxorubicin-loaded CQDs. This is because CQDs have excellent biocompatibility and may be easily absorbed by cells Surface modifications through covalent or electrostatic interactions can further improve drug loading efficiency and controlled release at the target site[132].

To advance CQDs as drug delivery vehicles, the development of stimuli-responsive nanocarriers is recommended. For example, CQDs integrated with charge-convertible polymers, such as PEG-(PAH/DMMA), can respond to the acidic tumor microenvironment, switching from anionic to cationic to facilitate drug release in the cytosol. Such systems, as demonstrated with cisplatin(IV)-loaded CQDs, exhibit enhanced antitumor effects with reduced side effects (see Figure 14) [134]. Additionally, CQDs' fluorescence properties enable real-time imaging, allowing for theranostic applications that combine therapy and diagnostics. Prioritizing biocompatible coatings and scalable synthesis methods, like solvothermal or hydrothermal approaches, will ensure safety and practicality for clinical translation.

For effective drug delivery, CQDs should be designed to carry a range of chemotherapeutic agents, including doxorubicin, cisplatin, and paclitaxel, while addressing challenges like poor solubility and non-specific distribution. By leveraging CQDs' large surface area and functionalization capabilities, drugs can be adsorbed or bonded non-covalently to achieve

systematic release at cellular levels. Research should focus on optimizing CQDs' stability and reducing potential cytotoxicity through surface passivation with biocompatible materials. These advancements position CQDs as a transformative platform for precise, efficient, and safe drug delivery in personalized medicine[132].
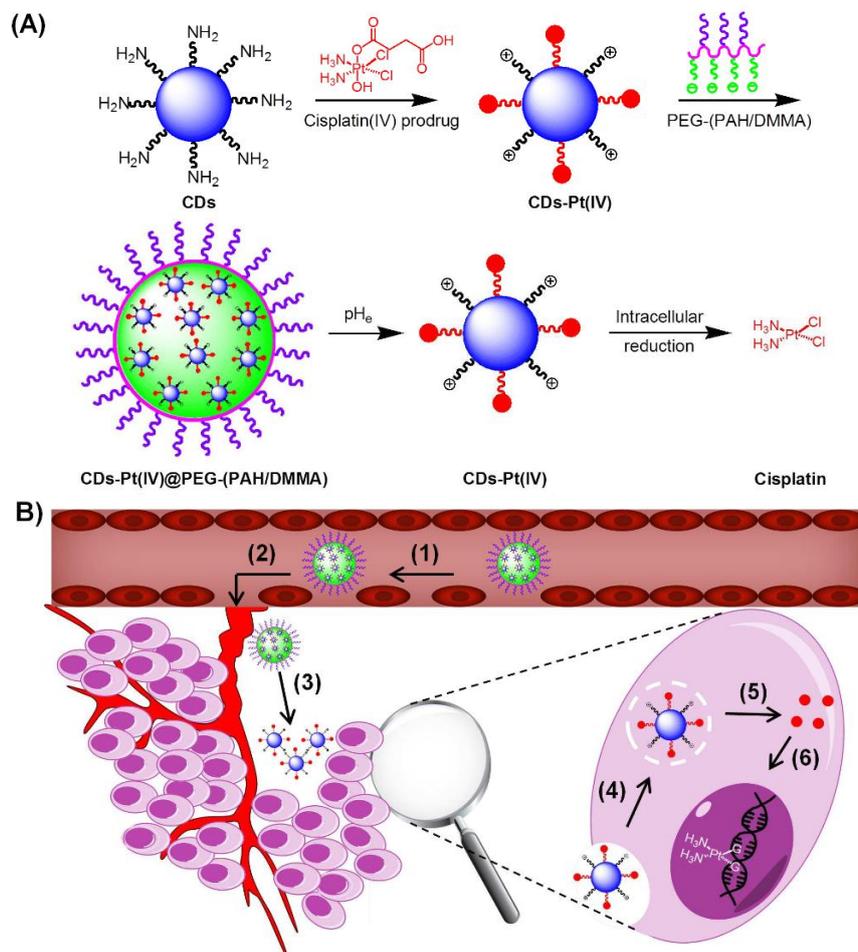

Fig.14 Illustrates the manufacturing and drug delivery system of a charge-convertible cyclodextrin-based nanocarrier, specifically CQDs–Pt(IV)@PEG-(PAH/DMMA) PAH: polyacrylamide hydrochloride; PEG: polyethylene glycol; DMMA: dimethyl maleic acid; pH_e: tumor extracellular pH. Longer circulation length (a); improved permeability and retention impact (b); reaction to extracellular pH of the tumor (c); endocytosis (d); decrease (e); and DNA binding (f) (Reprinted from Feng et al. [134]).

7.Conclusion

CQDs represent a groundbreaking advancement in nanotechnology, offering a unique combination of optical, chemical, and biological properties that enable their use across diverse fields. Their synthesis through top-down and bottom-up methods provides flexibility in tailoring their size, surface chemistry, and functionality, making them suitable for applications ranging from environmental sensing to targeted cancer therapies. The ability to characterize CQDs using advanced techniques like mass spectrometry, spectroscopy, and microscopy ensures precise control over their properties, enhancing their efficacy in bioimaging, optoelectronics, and drug delivery. As research progresses, CQDs are poised to overcome current limitations, such as cytotoxicity concerns, through improved functionalization and biocompatible coatings. With their potential to revolutionize personalized medicine, environmental monitoring, and energy-efficient technologies, CQDs stand as a cornerstone for

future innovations in nanotechnology, promising sustainable and impactful solutions to global challenges.

Funding

This research received no external funding

Ethical Statement

This research does not contain any studies with human or animal subjects performed by any of the authors

Data Availability Statement

 Not Applicable

Conflicts of Interest

 The authors declare no conflicts of interest

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