Chapter-1

1 Introduction and Literature Review

Nanomaterials, with their unique properties and promising applications, have revolutionized various scientific and technological fields. These materials typically characterized by their dimensions at the nanoscale (1-100 nm), exhibit distinct physical, chemical, and biological characteristics that differ from their bulk counterparts. Carbon, an element abundant on earth, exhibits remarkable properties and versatility compared to other substances. Its distinctive characteristics stem from the ability of carbon atoms to form single, double, and triple bond, facilitated by its electronic configuration of $1s^2\ 2s^2\ 2p^2$. These bonds utilize covalent contacts as well as weaker physical interactions such as Vander Waals forces, hydrophobic bond, π-π and cation-π bonds. Carbon achieves this versatility through three distinct hybridization states: sp^3 (tetrahedral, enabling single bonding), sp^2 (trigonal planar, enabling double bonding), and sp^1 (linear, enabling triple bond) [1]. Figure 1.1 illustrates various allotropes of carbon, including diamond, graphite, fullerene (C60, C70), amorphous carbon, carbon nanotube and graphene [2]. Notably, carbon exhibits a hydrogen, oxygen, nitrogen, and others. Carbon atoms readily form diverse types of compounds through bonding with each other. Consequently, carbon has been a subject of extensive scientific research for many decades, devoid of any controversial associations

[1]. [2]

1.1 Carbon Nanomaterials

Carbon nanomaterials are a distinct class of materials comprising carbon atoms arranged in nanoscale structures, encompassing carbon nanotubes, fullerenes, and graphene[3]. These materials possess exceptional properties, such as remarkable mechanical strength, high thermal and electrical conductivity, and significant surface area, rendering them valuable for diverse applications in electronics, energy storage, and biomedicine. One example of a carbon nanomaterial is graphene.

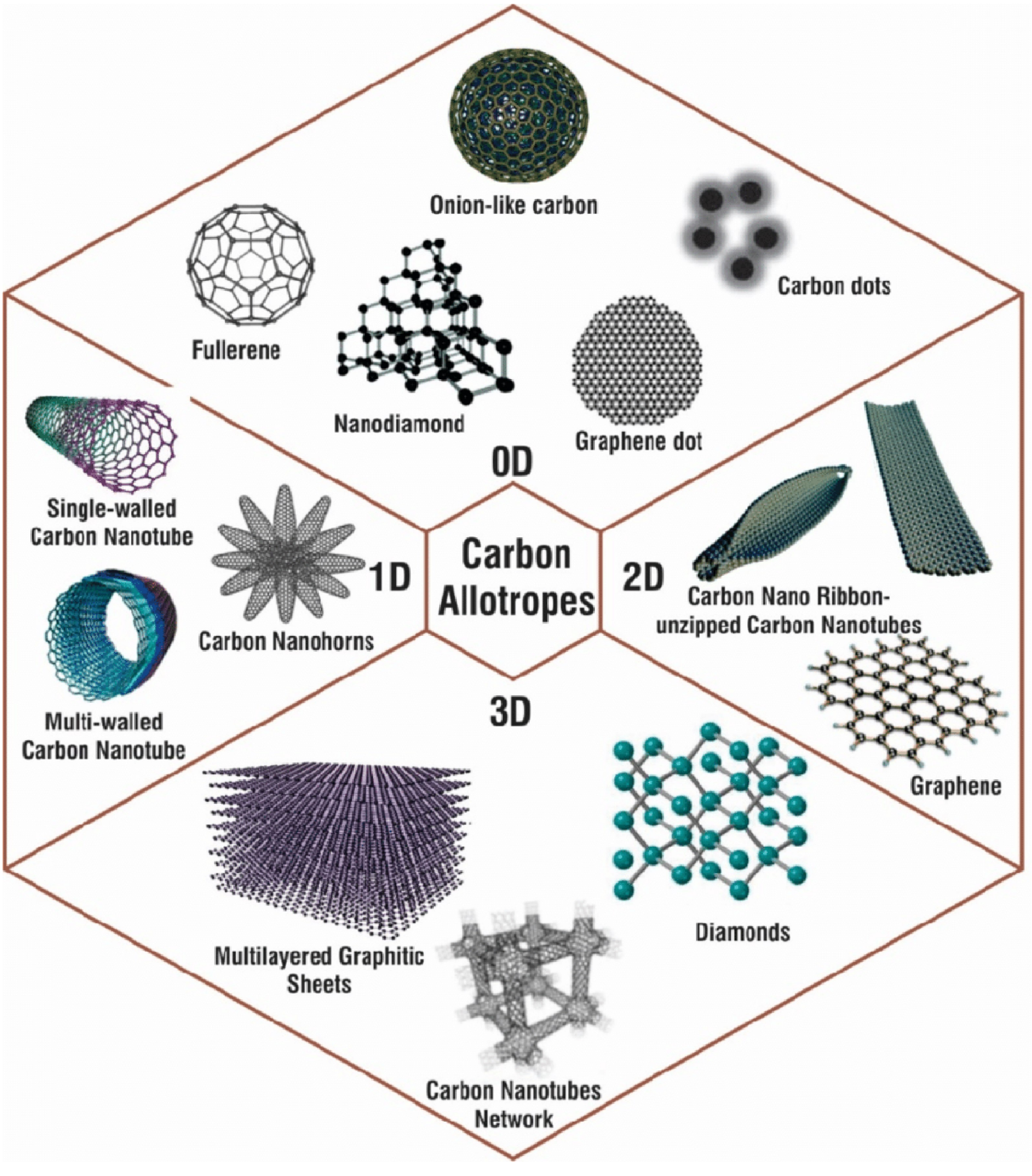

Figure 1. 1 Allotropes of carbon nanomaterials (*Materials, 2021,14, 5978*)

Graphene is a single layer of carbon atoms arranged in a hexagonal lattice. It has extremely high electrical conductivity, high mechanical strength, and high thermal conductivity[4]. Due to these properties, it has potential applications in fields such as electronics, energy storage, and sensors. Another example is Carbon nanotubes (CNTs) are cylindrical structures made of graphene sheets rolled up into a tube shape. CNTs have unique mechanical, electrical, and thermal properties, making them useful for various applications, such as in electronics, sensors, and energy storage devices[5]. They also have potential applications in fields like biomedical engineering, due to their small size and high surface area[6]. A third example is Fullerenes, which are carbon molecules composed of 60 or more carbon atoms arranged in the shape of a hollow sphere, ellipsoid, or tube. They are also known as "buckyballs." Fullerenes have potential applications in fields such as electronics, energy storage, and medicine[7]. Over the last two decades, carbon has emerged as a promising non-toxic alternative to highly fluorescent quantum dots. One such candidate, referred to as carbon quantum dots (CQDs), has garnered attention for its principal component.

1.1.1 Fullerene

Fullerenes were first discovered in 1985 by Sir Harold Kroto, Richard Smalley, and Robert Curl. They were awarded the Nobel Prize in Chemistry in 1996 for their groundbreaking discovery. Fullerenes are a unique form of carbon in which the carbon atoms are arranged in a hollow, cage-like structure, resembling a soccer ball[8]. The most well-known and studied fullerene is C60, which consists of 60 carbon atoms arranged in 20 hexagons and 12 pentagons, forming a spherical shape. Fullerenes are a class of carbon nanomaterials that are composed of carbon atoms arranged in the shape of a hollow sphere, ellipsoid, or tube[9]. The most common form of fullerene is the C60 molecule, which has the shape of a soccer ball and is often referred to as a "buckyball”[10]. Fullerenes can also have other numbers of carbon atoms, such as C70, C76, C78, C84, etc. Fullerenes have unique electronic and optical properties due to the arrangement of their carbon atoms in a closed cage structure[11]. They have a high electron affinity, which makes them useful in fields such as electronics and optoelectronics. They have been found to have potential applications in solar cells, field-effect transistors, and as a cathode material in lithium-ion batteries[7]. Fullerene derivatives are molecules that are based on the fullerene structure but have additional atoms or groups attached to the carbon cage. These derivatives can have different properties than the parent fullerene molecule and have potential applications in various fields such as medicine, electronics, and energy storage. One example of a fullerene derivative is a carboxy-fullerene, which is a fullerene molecule with carboxyl groups attached to its surface. These molecules have been found to have antioxidant properties and have potential applications in medicine as a treatment for neurodegenerative diseases[12]. Another example is endohedral fullerenes, which are fullerene molecules that have one or more atoms or molecules trapped inside the carbon cage. These molecules have unique electronic and optical properties and have potential applications in fields such as electronics, optoelectronics, and quantum computing[13]. Fullerene and its derivatives are actively researched and their potential applications are still being discovered. But due to the unique properties and possibilities of these carbon-based nanomaterials, it is expected that they will play a significant role in various fields in the future.

1.1.2 Graphene

In recent years, scientists Geim and Novoselov made a significant experimental finding about graphene, a one-atom-thick sheet of carbon atoms organized in a honeycomb pattern with exceptional mechanical and electrical capabilities. These scientists were awarded the Nobel Prize in Physics in 2010. Graphene is a two-dimensional (2D) material made up of a single layer of carbon atoms arranged in a hexagonal lattice. It has unique electronic and mechanical properties that make it useful in a wide range of applications[14], [15]. In terms of electronic properties, graphene has extremely high electrical conductivity due to its high mobility of charge carriers. This makes it a promising material for use in electronic devices such as transistors and solar cells. Its high surface area also makes it useful in energy storage applications, such as supercapacitors[16]. In terms of mechanical properties, graphene is an incredibly strong material. It has a tensile strength of over 130 gigapascals, making it about 100 times stronger than steel[17]. This makes it useful in applications such as composite materials and reinforced plastics. Graphene can also be combined with other materials to create different forms of two-dimensional (2D) materials, such as graphene-boron nitride heterostructures and graphene oxide. These different forms of 2D materials have unique electronic and optical properties that make them useful in various applications such as electronics, energy storage, and sensing[18]. When graphene is stacked together in multiple layers, it forms a three-dimensional (3D) material called graphite. Graphite has different properties than single-layer graphene, such as increased mechanical strength and increased thermal conductivity. This makes it useful in various applications such as lubricants, batteries, and fuel cells[19].

1.1.3 Carbon Nanotube

The discovery of carbon nanotubes (CNTs) can be traced back to the early 1990s, although their existence was theoretically predicted even earlier[20]. In 1991, Sumio Iijima, a Japanese physicist, successfully isolated and characterized multi-walled carbon nanotubes (MWNTs) using a high-resolution transmission electron microscope. Shortly after, he also identified single-walled carbon nanotubes (SWNTs) in 1993[21]. Carbon nanotubes are cylindrical structures made up of carbon atoms arranged in a hexagonal lattice. They can be thought of as rolled-up graphene sheets, and their properties are highly dependent on their atomic arrangement and diameter[22]. These nanotubes can be single-walled (consisting of one layer of carbon atoms) or multi-walled (multiple concentric layers of carbon atoms)[23]. Single-walled carbon nanotubes (SWCNTs) have a diameter of around 1 nm and a length of several micrometres. They have unique electronic and mechanical properties due to their cylindrical shape and the way their carbon atoms are arranged. SWCNTs can have metallic or semiconducting properties, depending on their chirality, or the way they are rolled up[23]–[25]. Due to their unique properties, SWCNTs have potential applications in various fields such as electronics, energy storage, and sensors. For example, their high electrical conductivity and mechanical strength make them useful in electronics and sensors, while their high surface area makes them useful in energy storage applications such as supercapacitors[26].

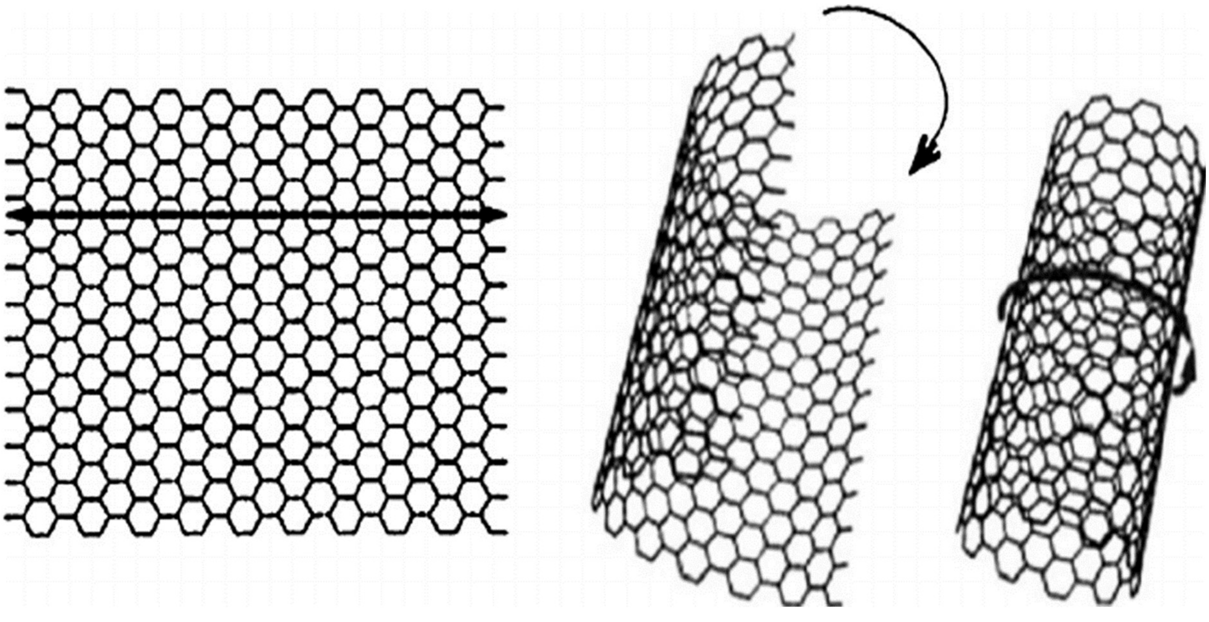

Figure 1. 2 Graphene folding to make CNT (*Int. J Biological Macromolecules, 2013, 58, 1-6*).

On the other hand, multi-walled carbon nanotubes (MWCNTs) have multiple concentric layers of graphene rolled up into a tube shape. They have a diameter of around 10 nm and a length of several micrometres[27], [28]. MWCNTs have unique mechanical and thermal properties due to their layered structure. They have a high strength and stiffness, making them useful in composite materials and reinforced plastics[29]. MWCNTs also have high thermal conductivity, making them useful in thermal management applications such as heat dissipation in electronic devices. They also have a large surface area and high chemical reactivity which makes them useful in catalytic applications[30].

Carbon nanotubes are formed by rolling a graphene sheet in various directions, resulting in different structures with metallic or semiconducting properties (Figure 1.2)[31]. The characteristics of nanotubes can be described using two vectors: the circumferential vector **($\mathbf{C_h}$)** and the translational vector **(T)**, which form the unit cell of the nanotube. $\mathbf{C_h}$ is the vector along the tube surface that connects two carbon atoms of equal mass and can be expressed as $\mathbf{C_h = na_1 + ma_2}$, where $\mathbf{a_1}$ and $\mathbf{a_2}$ are graphite basis vectors, and **n** and **m** are integers. The chiral angle ($\theta = \tan^{-1}[\sqrt{3}\ n/(2m + n))]$) characterizes the nanotube and can be used to classify them into three categories based on their electronic properties: armchair, zigzag, and chiral (Figure 1.3)[32].

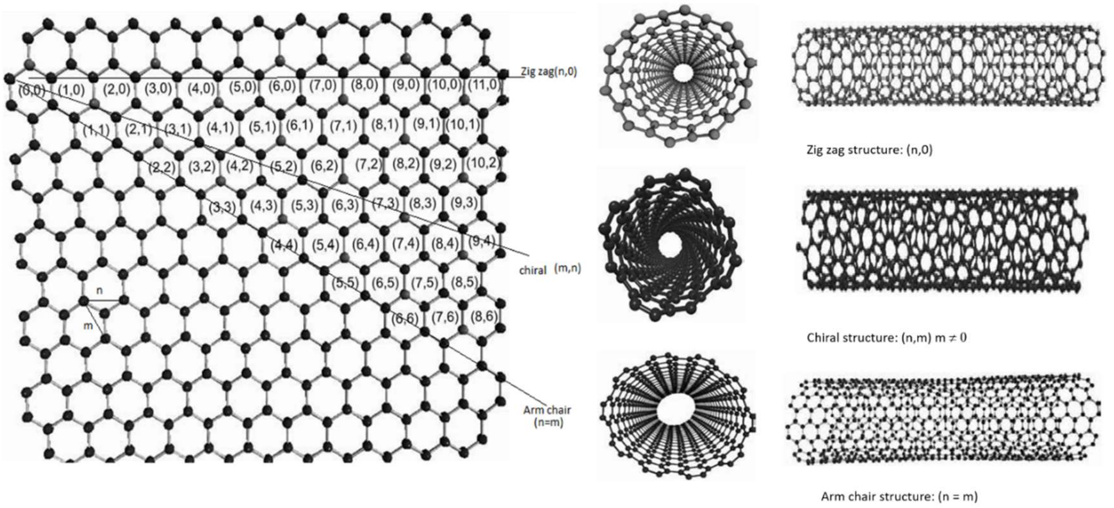

Figure 1. 3 Single layered graphene sheet with integer labels (n, m). Types of CNTs knowing the numbers, the diameter and chiral angle may be determined (n, m) (*Nanoscale, 2010, 2, 373-380*).

Armchair nanotubes have the chiral angle of 30° and are metallic in nature. They are degenerate semimetals with a zero-band gap. Zigzag nanotubes have a chiral angle of 0° and are also metallic if $m = 0$ and $n > 0$. They have a finite band gap if $(n - m)/3$ is an integer (I), where $m \neq n$. Otherwise, they are semiconducting. Chiral nanotubes have chiral angles between 0° and 30° and exhibit varied electronic properties[33]. They are metallic if $(n - m)/3 = I$ (I being an integer and $m \neq n$), and semiconducting if not. The band gap of these nanotubes is inversely proportional to their diameter, which in turn determines their electronic characteristics. This relationship between chiral angle, diameter, and band gap is what defines the electronic behaviour of carbon nanotubes[34].

1.2 Carbon Quantum Dots

Carbon quantum dots (CQDs) are nanoscale carbon-based materials with sizes typically ranging from 1-10 nm[34]–[36]. They possess unique properties that are distinct from bulk carbon materials due to quantum confinement effects, surface functionalization, and edge effects. These properties make CQDs highly attractive for various applications, including optoelectronics, biomedicine, sensing, and more[37], [38]. Functionalization of carbon quantum dots (CQDs) refers to the process of modifying the surface of CQDs with chemical groups or molecules. This process is usually done to improve the solubility and dispersibility of CQDs in different solvents and to modify their properties for specific applications[39]. Functional groups that can be added to CQDs include carboxylic acid, hydroxyl, amino, and thiol groups. These groups can be used to improve the solubility and dispersibility of CQDs in different solvents, as well as to modify their electronic and optical properties[35]. Functionalized CQDs have many potential applications in various fields such as biomedical engineering, electronics, energy storage, and sensing[40]. For example, CQDs functionalized with carboxylic acid groups have been found to have antioxidant properties and have potential applications in medicine as a treatment for neurodegenerative diseases[41]. CQDs functionalized with thiol groups have been found to have high conductivity and have potential applications in electronics[42]. Compared to other nanomaterials, CQDs have unique properties that make them useful in a wide range of applications. They have a high absorption coefficient, high photoluminescence quantum yield, and a broad absorption spectrum, which makes them useful in optoelectronic applications such as LEDs and solar cells[43]. They also have excellent biocompatibility, which makes them useful in biomedical applications such as drug delivery and imaging[44]. In addition, CQDs are also more stable and less toxic than other similar nanomaterials, such as quantum dots, which can be made of heavy metals and have toxicity issues[45].

Overall, functionalization of carbon quantum dots (CQDs) refers to the process of modifying the surface of CQDs with chemical groups or molecules, with the goal of improving the solubility and dispersibility of CQDs in different solvents and to modify their properties for specific applications[46]. Functionalized CQDs have many potential applications in various fields such as biomedical engineering, electronics, energy storage, and sensing[47].

1.2.1 Synthesis Methods of CQDs

Carbon Quantum Dots (CQDs) are nanoscale carbon-based materials that exhibit unique optical, electronic, and chemical properties. They have gained significant attention in various fields, including optoelectronics, sensing, imaging, and bio applications. The synthesis methods of CQDs can be broadly categorized into two main approaches: top-down and bottom-up methods[47].

1.2.1.1 Top-Down Synthesis Methods

The top-down approach involves breaking down larger carbon-based materials into smaller CQDs. This can be done through physical or chemical methods, such as mechanical grinding, sonication, or chemical oxidation. An example of a top-down approach is the synthesis of CQDs from graphite by mechanical grinding. **Electrochemical Exfoliation,** in this method the graphite electrodes are subjected to electrolysis in an appropriate solvent. The high voltage applied leads to the exfoliation of graphite layers, generating CQDs in the process[48]. **Laser Ablation** involves the use of high-energy lasers to vaporize a carbon target in a controlled environment. The vaporized carbon then condenses and forms CQDs[49]. **Mechanical Ball Milling,** in this method the mechanical forces generated by ball milling equipment break down larger carbon materials into smaller fragments, eventually leading to the formation of CQDs[50].

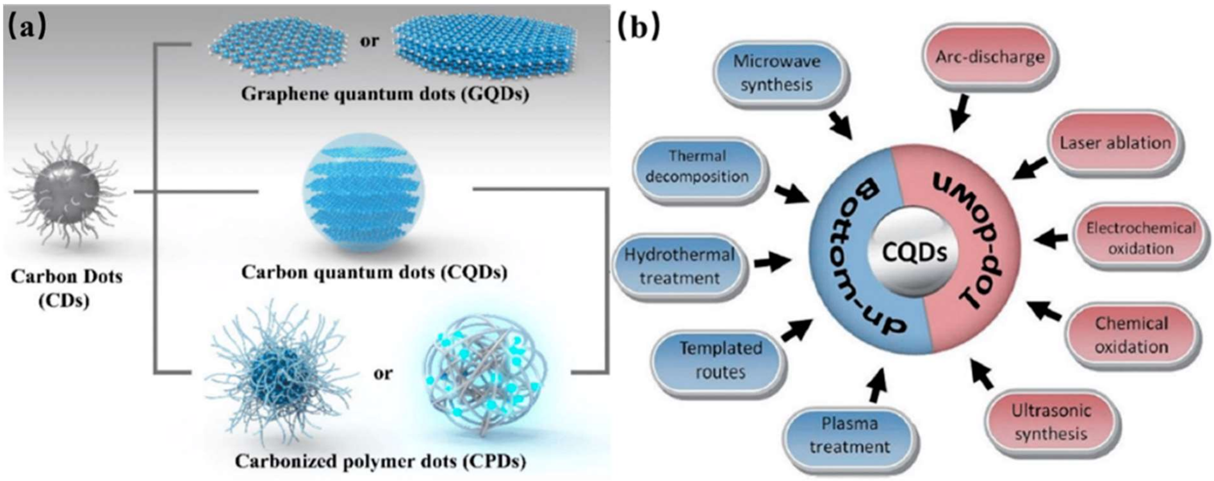

Figure 1. 4 (a) Synthesis process and structure of CQDs, (b) Different synthesis techniques of Top-Down and Bottom- Up (*Nanomaterials 2021, 11, 3419*)

1.2.1.2 Bottom-Up Synthesis Methods

Bottom-up methods involve the controlled assembly or synthesis of CQDs from smaller molecular precursors or carbon-containing compounds. **Hydrothermal/Solvothermal**

Synthesis, this is one of the most common methods for CQD synthesis. Precursor molecules, often containing carbon and heteroatom (such as nitrogen or oxygen), are dissolved in a solvent and then heated under high pressure in a hydrothermal reactor[51], [52]. The reaction promotes the nucleation and growth of CQDs. CQDs were prepared by the hydrothermal method using a Teflon-lined autoclave and furnace. In this method, carbon compounds are heated at high temperature and pressure, forcing the precursor molecules to interact with water molecules. When a mixture was heated, the pressure increased, resulting in deoxygenation of the water molecules. The carbon layers were repelled by the production of H+ and OH ions. However, the high-pressure conditions can be managed by using a stainless-steel autoclave with Teflon walls. Self-assembly can be used to produce CQDs by oxidizing carbon sheets to generate additional oxygen-containing functional groups. During the process, the size of the CQDs was reduced, resulting in high fluorescence emission[53]. The hydrothermal process can yield a significant amount of quantum dots with homogeneous particle size distribution. High production yield is important because it can help to improve the photoluminescent properties of the CQDs through stronger surface passivation[54]. Various Forms of Biomass Serve as Carbon Precursors for CQD Synthesis and applications listed below Table.

Biomass	**Q.Y.**	**PL**	**Application**	**Ref.**
Banana Leaves		Blue, Red	Mercury and Arsenic detection	[55]
Coriander	6.48	Blue	Antioxidants, bio-imaging	[56]
Chitosan	13	Blue	Nitro aromatics detection	[57]
Watermelon	7.1	Blue	Optical imaging probe	[58]
Tamarind leaves	46.6	Blue	Mercury detection	[59]

Sweet lemon		Green	Gene therapy and breast cancer detection	[60]
citric acid and 2,3-diinonaphthalene	70	Green	Dye sensitized solar cell	[61]
Grass		Green	Removing water pollutants	[62]
Pineapple peel	0.42	Blue	Sensor, memory devices, mercury detection	[63]
Rice residue and glycine	23.48		Heavy metal detection	[64]

Table 1. 1 Various Forms of Biomass Serve as Carbon Precursors for CQD Synthesis and applications.

Microwave-Assisted Synthesis is used to rapidly heat precursor solutions, promoting nucleation and growth of CQDs. This method typically yields CQDs in a shorter timeframe compared to traditional heating methods[65]. **Sol-Gel Method,** in this method a precursor solution containing carbon and other components is hydrolysed and polymerized to form a gel-like material. Subsequent heat treatment or chemical processing then leads to the formation of CQDs[66]. **Pyrolysis,** in this method the organic precursors such as sugars or small molecules, are heated at high temperatures in the absence of oxygen. This results in the decomposition and reorganization of the precursors into CQDs[67]. **Chemical Vapor Deposition (CVD),** in CVD the carbon-containing precursor gases are introduced into a reactor where they decompose and deposit as CQDs on a substrate. This method is commonly used to synthesize CQDs on solid surfaces[68]. **Electrochemical Synthesis** involve the controlled electrochemical reduction of carbon-containing compounds. CQDs can be synthesized on electrode surfaces or in solution using this approach[69]. Each of these methods has its advantages and limitations, influencing factors like size, morphology, surface functionalization, and optical properties of the resulting CQDs. Researchers often choose synthesis methods based on their specific application requirements and desired CQD properties.

1.2.1.3 Green Synthesis Methods

Green synthesis methods are environmentally friendly approaches used to produce nanoparticles and other materials. These methods typically involve the use of natural or sustainable resources and reduce the generation of hazardous waste[70]. One popular application of green synthesis is in the production of gold nanoparticles (AuNPs)[71]. Here, I will provide a scientific overview of the green synthesis of gold nanoparticles and its advantages.

Method: One common green synthesis method for gold nanoparticles involves the use of plant extracts, such as those from medicinal plants or fruit peels. Here's a simplified step-by-step process.

Step-1. Collection of plant materials: Select a suitable plant source, such as Tulsi, Vinca, Aloe vera, green tea, or citrus fruit peel.

Step-2. Preparation of Extract: Crush or grind the plant material to create a fine powder. Then, extract the bioactive compounds by immersing the powder or plant leaves in a suitable solvent, often water or ethanol. Heat or sonication may be used to facilitate extraction.

Step-3. Reduction of gold salt: Prepare a solution of gold salt, typically chloroauric acid (HAuCl4), in a solvent. Mix the plant extract with the gold salt solution.

Step-4. Nanoparticle Formation: The bioactive compounds in the plant extract, which may include polyphenols, flavonoids, or other reducing agents, reduce the gold ions (Au^{3+}) to form gold nanoparticles. This reduction process is typically monitored by observing a color change from yellow to red or purple.

Step-5. Characterization: The synthesized gold nanoparticles can be characterized using techniques like UV-VIS spectroscopy, TEM (Transmission Electron Microscopy), and XRD (X-ray Diffraction) to determine their size, shape, and crystalline structure.

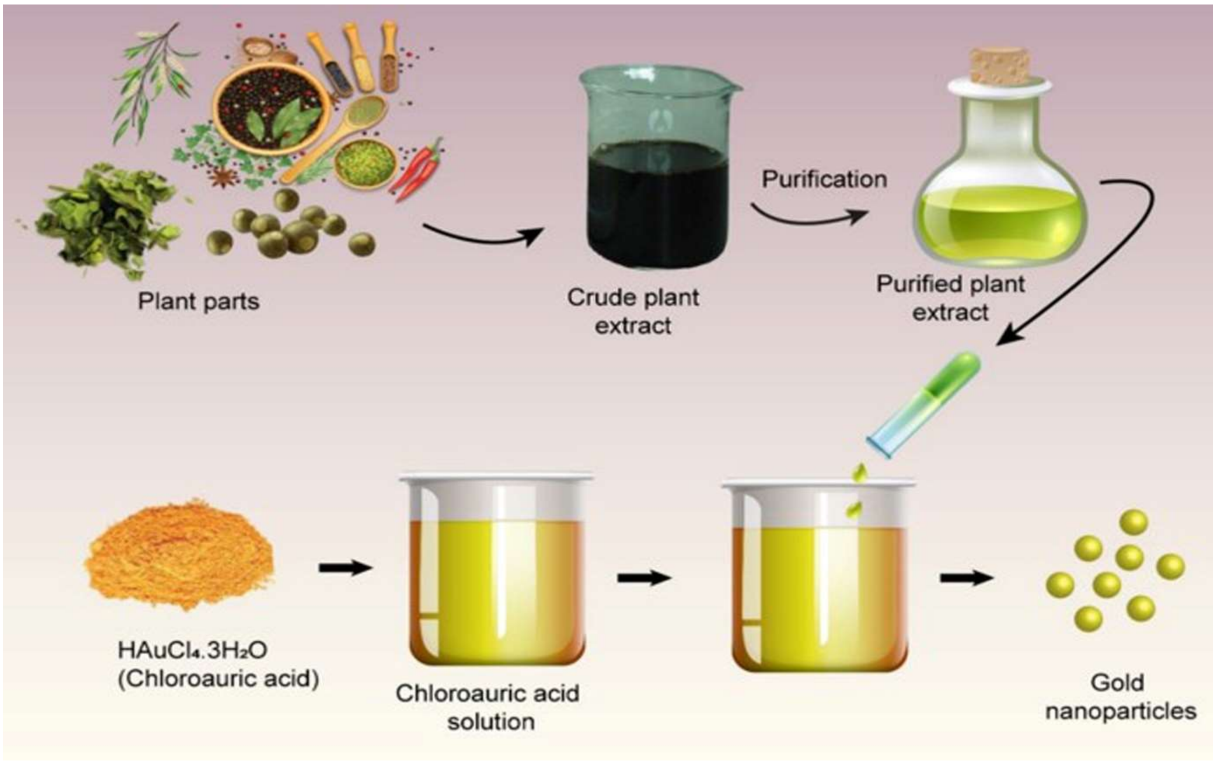

Figure 1. 5 Green synthesis of gold nanoparticles (GNPs) (*Molecules, 2022, 27, 1391*).

Many Advantages of green synthesis method obtained[70], [72], [73]. **Environmentally Friendly**, this method used natural resources and avoid harmful chemical, making them environmentally sustainable. **Biocompatibility**, the green synthesized nanoparticles often biocompatible in nature, making them suitable for medical and biological applications. **Cost-Effective**, many plant extracts are readily available and cost-effective, reducing the overall production cost of gold nanoparticles. **Tunable Properties**, the size and shape of gold nanoparticles can be controlled by adjusting the reaction conditions, allowing for tailoring of their properties for specific applications.

1.2.1.4 Surface Modification of CQDs

Surface modification of carbon quantum dots (CQDs) is a process that involves modifying the surface chemistry of the CQDs to improve their properties or to make them suitable for a specific application[74], [75]. There are several methods for surface modification of CQDs, including chemical modification, physical adsorption, and covalent modification. **Chemical modification:** This method involves the modification of the surface of the CQDs by introducing functional groups, such as carboxylic acid, amine, or hydroxyl groups, through chemical reactions. This can be done through chemical oxidation of the CQDs or by exposing the CQDs to a solution of a chemical reagent. For example, CQDs can be modified with carboxylic acid groups through a chemical oxidation process using nitric acid[76], [77]. **Physical adsorption:** This method involves the adsorption of molecules or nanoparticles onto the surface of the CQDs. For example, CQDs can be modified with a biomolecule, such as an antibody or a protein, through a physical adsorption process[78]. **Covalent modification:** This method involves the covalent bonding of molecules or nanoparticles onto the surface of the CQDs[79]. For example, CQDs can be modified with a biomolecule, such as an antibody or a protein, through a covalent modification process. Surface modification of CQDs can improve their properties, such as solubility, stability, and biocompatibility, and make them suitable for a specific application such as bio-imaging, sensing, and drug delivery. For example, CQDs modified with a carboxylic acid group can be more stable in an aqueous environment and have a higher solubility. CQDs modified with a biomolecule, such as an antibody or a protein, can be used as a biosensor or for targeted drug delivery[80]. CQDs can be easily doped with heteroatoms, which increases their solubility and facilitates their surface functionalization. The presence of various functional groups on the CQDs surface consisting of multiple atoms such as carbon, hydrogen, nitrogen, oxygen, etc., enhance dispersion in water and facilitate further functionalization and surface passivation[81]. Two distinct N-doped carbon quantum dots (CQDs) were produced using l-glutamic acid as a precursor in a one-step hydrothermal process at 230 and 250 °C. Hydrothermally produced NCQDs from chitosan. When ethanol precipitation was employed to purify, 85.3% product yield was achieved[82]. One example of surface modification of carbon quantum dots (CQDs) is the modification with carboxylic acid groups. This can be achieved through chemical oxidation of the CQDs using nitric acid[83]. In this process, CQDs are suspended in a solution of nitric acid and heated to a high temperature. The nitric acid reacts with the CQDs to introduce carboxylic acid groups on the surface of the CQDs. Another example is the modification of CQDs with a biomolecule, such as an antibody or a protein. This can be achieved through physical or covalent adsorption. In this process, CQDs are suspended in a solution containing the biomolecule, and the mixture is agitated for a period of time. The biomolecule adsorbs onto the surface of the CQDs through non-covalent interactions or covalent bonding. The modified CQDs with carboxylic acid group are more stable in an aqueous environment and have a higher solubility which makes them more suitable for applications such as bio-imaging, sensing, and drug delivery.

1.2.2 Properties of CQDs

1.2.2.1 UV-VIS Absorption Properties of CQDs

The ultraviolet-visible (UV-Vis) absorption properties of carbon quantum dots (CQDs) are determined by the electronic transitions of the n- π^* and π- π^* transitions in the carbon atoms of the CQDs[84]. The π- π^* orbitals are responsible for the characteristic absorption spectrum of CQDs, which spans the UV-Vis range. The absorption spectrum of CQDs typically has a broad band in the UV-Vis range with a peak at around 230-500 nm, which is due to the transitions of the π and π* orbitals. The position and shape of the peak in the absorption spectrum can vary depending on the size, shape, and structure of the CQDs, as well as the surface chemistry of the CQDs[85]. The π-states of CQDs can be ascribed to aromatic sp^2-hybridized carbons in their core. The degree of absorption increased exponentially with increasing diameters. The absorption peak at about 230 nm was attributed to the π-π* transition of C=C bonds, whereas the absorption peak at approximately 298 nm was related to the n-π* transition of C=O bonds formed during the hydrothermal process[86], [87]. CQDs synthesized from graphene oxide by a hydrothermal process have been found to have an absorption peak at around 300 nm. This peak is attributed to the transitions of the π-π*orbitals in the carbon atoms of the CQDs[88]. CQDs synthesized from carbon black by a microwave-assisted process, have been found to have an absorption peak at around 400 nm, this is due to the transitions of the π-π*orbitals in the carbon atoms of the CQDs[81].

The high extinction coefficient of CQDs, which is the ability to absorb a large amount of light at a given wavelength, makes them useful as photoluminescent materials, as they are able to convert absorbed light into emitted light, known as fluorescence. CQDs also have a high quantum yield, which is the ratio of the number of emitted photons to the number of absorbed photons[83]. This property makes CQDs useful as fluorescent probes in bioimaging, sensing, and other optoelectronic applications.

1.2.2.2 Photoluminescence Properties of CQDs

Photoluminescence (PL) properties of carbon quantum dots (CQDs) refer to the ability of CQDs to emit light upon excitation by an external energy source. CQDs have unique and tuneable photoluminescence properties, which are determined by their size, shape, and surface chemistry[36], [83]. CQDs have a broad and strong photoluminescence spectrum, which spans the visible and near-infrared (NIR) regions of the electromagnetic spectrum. The PL spectrum of CQDs typically has a peak at around 400-800 nm, which is due to the transitions of the π-π* orbitals in the carbon atoms of the CQDs. The position and shape of the peak in the PL spectrum can vary depending on the size, shape, and structure of the CQDs, as well as the surface chemistry of the CQDs[89]. CQDs also have a high quantum yield, which is the ratio of the number of emitted photons to the number of absorbed photons. This property makes CQDs useful as fluorescent probes in bioimaging, sensing, and other optoelectronic applications[90]. The high quantum yield of CQDs is due to their small size, which allows for efficient energy transfer from the excited state to the ground state, and their high surface-to-volume ratio, which allows for efficient light emission[40].

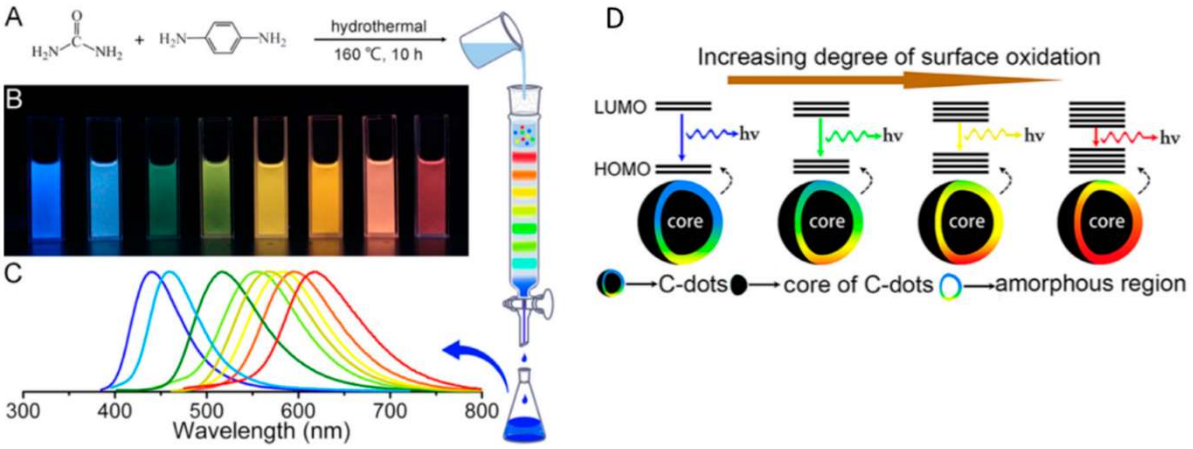

Figure 1. 6 (A) synthesis and purification of CQDs (B) CQDs samples under UV-light (365 nm), (C) PL spectra at different wavelength, and (D) Tuneable emission spectra of CQDs with different degree of oxidation. (*ACS Nano 2016, 10, 1, 484–491*).

The photoluminescence properties of CQDs can also be tuned by modifying their surface chemistry. For example, CQDs modified with carboxylic acid groups have been found to have a red-shifted PL spectrum, which makes them useful for NIR bioimaging applications[39]. CQDs modified with biomolecules, such as antibodies or proteins, have been found to have a high specificity and high sensitivity for bio-sensing applications. Consequently, CQDs with a fixed chemical composition can emit fluorescence at different wavelengths if their sizes differ as shown in Figure 1.6.

The surface state of a CQDs is made up of the functional groups on the carbon dots and any surface defects. The HOMO is the highest energy orbital that is occupied by electrons in the CQDs, while the LUMO is the lowest energy orbital that is unoccupied by electrons. The energy difference between the HOMO and the LUMO is known as the bandgap, and it determines the optical properties of the CQDs. The HOMO and LUMO of CQDs are primarily composed of π-π^* orbitals, which are formed by the hybridization of the 2s and 2p orbitals of carbon atoms. The degree of hybridization of these orbitals can affect the energy levels of the HOMO and LUMO, and thus the bandgap energy of the CQDs[91]. For example, CQDs with a higher degree of hybridization will have a smaller bandgap energy, which means that they will absorb light at a lower energy and emit light at a higher energy[92]. Hybridization can also affect the shape and symmetry of the HOMO and LUMO, and thus the optical properties of the CQDs. For example, sp^2 hybridization of carbon atoms in CQDs leads to the formation of planar graphene-like structures, which have a strong absorption in the visible region and a strong fluorescence in the near-infrared (NIR) region. On the other hand, sp3 hybridization of carbon atoms in CQDs leads to the formation of three-dimensional fullerene-like structures, which have a strong absorption in the ultraviolet (UV) region and a weak fluorescence in the visible region[93]. When sp^3 structures break up the sp^2 hybridized carbon domain, surface defects in electronic conjugations happen. Between the HOMO and LUMO core states, these surface states add a lot of energy levels and transitions, which makes the emission peaks wider[94].

1.2.2.3 Chemiluminescence

Chemiluminescence is the emission of light as a result of a chemical reaction. In the context of carbon quantum dots (CQDs), chemiluminescence refers to the ability of CQDs to emit light upon the addition of a chemical reagent or under certain conditions, such as pH or temperature changes[95]. The mechanism of chemiluminescence in CQDs is based on the excitation of the CQDs by a chemical reagent, which causes the electrons in the CQDs to transition from the ground state to the excited state. The excited electrons then relax back to the ground state, emitting light in the process. Chemiluminescence (CL) properties of CQDs are affected by a number of factors, including the size and shape of the CQDs, the surface chemistry of the CQDs, and the concentration and properties of the chemical reagents. For example, CQDs modified with carboxylic acid groups have been found to have a pH-dependent chemiluminescence, where the intensity of the chemiluminescence increases as the pH decreases[96]. CQDs modified with biomolecules, such as antibodies or proteins, have been found to have a high specificity and high sensitivity for bio-sensing applications[97]. The chemiluminescent properties of CQDs have been widely studied for their potential in various applications such as bio-imaging, sensing, catalysis, and energy storage.

1.2.2.4 Up-conversion photoluminescence (UCPL)

Up-conversion photoluminescence (UCPL) refers to the phenomenon where lower energy photons are absorbed by a material and then re-emitted as higher energy photons[98]. This process is in contrast to the more common down conversion process, where higher energy photons are absorbed and then re-emitted as lower energy photons. In the context of carbon quantum dots (CQDs), up-conversion photoluminescence (UCPL) refers to the ability of CQDs to absorb two or more lower energy photons and then re-emit a higher energy photon. This process is made possible by the presence of rare earth ions such as Er^{3+} or Yb^{3+} that are incorporated into the CQDs[99]. These ions act as the energy transfer mediator, and they have the ability to absorb the lower energy photons and then transfer the energy to the CQDs, where it is re-emitted as a higher energy photon. The intensity of the UCPL from CQDs is affected by a number of factors, including the size and shape of the CQDs, the surface chemistry of the CQDs, the concentration and properties of the rare earth ions, and the excitation wavelength and intensity. UCPL properties of CQDs have been widely studied for their potential in various applications such as bio-imaging, sensing, catalysis, and energy storage. For example, CQDs with UCPL properties have been used in bio-imaging applications by using two-photon excitation, which allows for deeper imaging into biological tissue[100]. In sensing applications, CQDs with UCPL properties have been used to detect certain analytes by measuring the change in intensity of the UCPL in the presence of the analyte. Another exciting element of CQDs that is being researched is the **photo-induced electron transfer property (PET)**[101]. CQDs have been examined for photo-response, electron transfer and photo-induced charge separation processes as they have an active electron accepting/ donating surface[102]. Such efforts are bound to advance the existing mechanistic understanding and many applications in catalysis and related light-energy conversion reactions.

1.2.3 Application of CQDs

CQDs exhibit good biocompatibility, low cost, and unique optical properties and mechanical properties, such as high fluorescence stability, broad and tuneable excitation and emission spectra, CQDs have a wide range of potential applications[40], [53], [102].

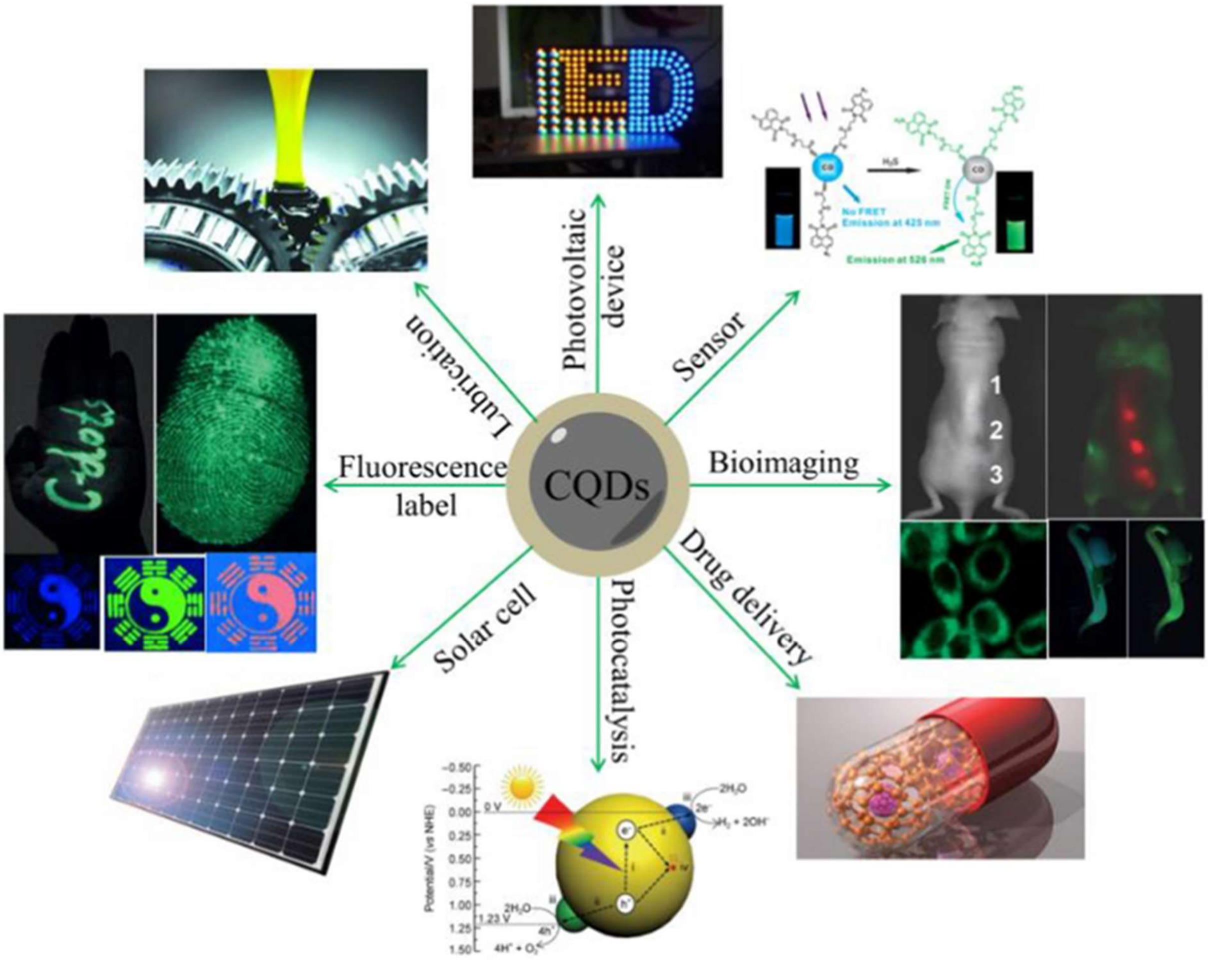

Figure 1. 7 Various application of carbon quantum dots (CQDs) (*Journal of Materials Science, 2021, 56, 1-32*).

Some of the key applications include as display technology, solar cell, bioimaging, sensors, photocatalysis, optoelectronic, anticancer, and many more applications (Figure 1.7).

1.2.3.1 Chemical Sensing Application

Chemical sensing is one of the important application areas for carbon quantum dots (CQDs) due to their unique optical and electronic properties. CQDs have been used in a wide range of chemical sensing applications, including sensing of gases, biomolecules, and environmental pollutants. **Gas Sensing:** Gas sensing is one of the important application areas for carbon quantum dots (CQDs) due to their unique optical and electronic properties. CQDs have been used as the sensing layer in gas sensors to detect a wide range of gases, such as carbon monoxide, ammonia, nitrogen oxides, and volatile organic compounds[103]. One example of a gas sensing application using CQDs is the detection of carbon monoxide (CO). Carbon monoxide is a toxic gas that is colorless, odorless, and tasteless, making it difficult to detect. CQDs have been used as the sensing layer in CO sensors due to their high sensitivity and selectivity. The sensing mechanism typically involves the adsorption of CO molecules on the surface of the CQDs. This causes a change in the optical properties of the CQDs, such as a shift in the absorption or emission spectra. By monitoring the changes in the optical properties of the CQDs, it is possible to detect the presence of CO at low concentrations[104]. One example of a high performance of CO gas sensor based on a novel PEDOT: PSS/PPA nanocomposite. The nanocomposite was deposited onto a copper electrode substrate and then exposed to different concentrations of CO. Keithley 2400 was used to record the current–voltage (*I–V*) characteristics and all sensing measurements of PEDOT: PSS and PEDOT: PSS/PPA at ambient temperature. The sensor's electrical resistance was measured using Keithley-4200 for the real-time monitoring of the resistance and current of the sensor when exposed to various concentrations of target gases[104]. Another example of a CQD-based gas sensor is a device that utilizes CdS/ZnS core/shell CQDs for sensing of nitrogen oxides (NOx)[105]. **Biomolecule Sensing:** Biomolecule sensing is another important application area for carbon quantum dots (CQDs) due to their unique optical and electronic properties. CQDs have been used as fluorescent probes in biosensors to detect biomolecules such as DNA, proteins, and small molecules[54]. One example of a biomolecule sensing application using CQDs is the detection of DNA. DNA is the genetic material that carries the genetic instructions for the development and function of all living organisms. The detection of DNA is important in various fields such as medical diagnostics, forensic science, and genetic engineering. A common method for detecting DNA is by using fluorescent dyes that bind specifically to the DNA, and then measuring the fluorescence signal. However, these dyes can suffer from quenching, photobleaching, and cross-talk issues, which limit their sensitivity and specificity[106]. CQDs have been used as an alternative to fluorescent dyes for DNA detection due to their high quantum yield and narrow emission spectra. One example of a ultrasensitive label free DNA detection based on solution gated graphene transistor functionalised with CQDs[107]. **Environmental Sensing:** Environmental sensing is another important application area for colloidal quantum dots (CQDs) due to their unique optical and electronic properties. CQDs have been used to detect environmental pollutants such as heavy metals, pesticides, and organic pollutants[108].

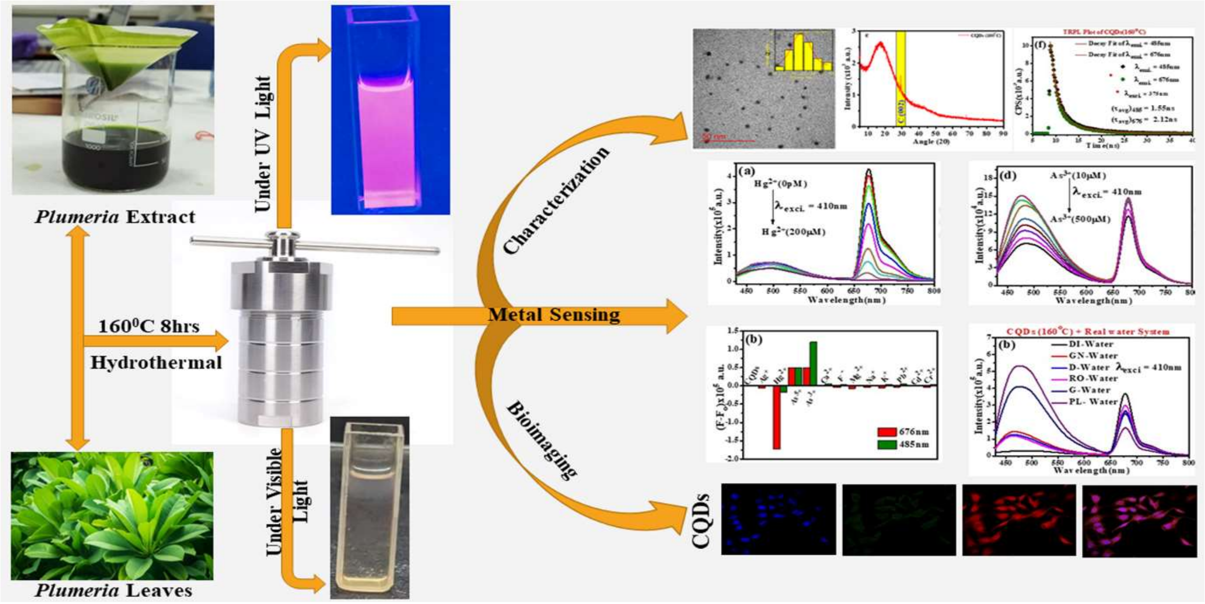

Figure 1. 8 Plumeria leaves extract used for the synthesis of CQDs for the application of metal sensing and bioimaging.

One example of an environmental sensing application using CQDs is the detection of heavy metals. Heavy metals are a group of elements with high atomic weight and high density, and are toxic to living organisms. The detection of heavy metals is important in various fields such as environmental monitoring, industrial waste management, and water purification. CQDs have been used as an alternative to these methods for heavy metal detection due to their high quantum yield and narrow emission spectra. Numerous plant-derived CQDs have been used to detect metal ions in water, including Lotus root for Hg^{2+} and cell imaging[109], Strawberry for Hg^{2+}[110], Bamboo leaves for Pb^{2+} and Hg^{2+}[111], Jackfruit seeds for Au^{3+}[112], Papaya for Fe^{3+}[113], Mung bean for detecting Fe^{3+}[114], and Tulsi leaves for Cr^{4+} detection[115], Banana and Plumeria leaves used for Hg^{2+} and As^{3+} detection and bioimaging[55].

1.2.3.2 Optoelectronic Application

Optoelectronic applications of CQDs refer to the use of CQDs in devices that convert light energy into electrical energy or electrical energy into light energy. CQDs have unique optical and electronic properties that make them attractive for a variety of optoelectronic applications[38]. Some examples of optoelectronic applications of CQDs include. **Solar cells** are devices that convert sunlight into electrical energy, and carbon quantum dots (CQDs) have been explored as a potential active material for solar cell fabrication due to their unique optical and electronic properties. CQD-based solar cells are typically fabricated using a process called "quantum dot sensitized solar cells" (QDSSCs). CQD-based solar cells have shown promise as a low-cost alternative to traditional silicon-based solar cells[116]. They have high absorption coefficients and tunable bandgaps, which allow them to absorb a wide range of light wavelengths and convert more sunlight into electrical energy. Additionally, CQDs have been functionalized with various molecules to improve their solubility and stability, which is essential for solar cell applications.

CQDs have been used as the active material in **Light emitting diode** (LEDs) due to their high quantum yield, narrow emission spectra, nontoxic, ecofriendly, inexpensive, and color tunability[117].

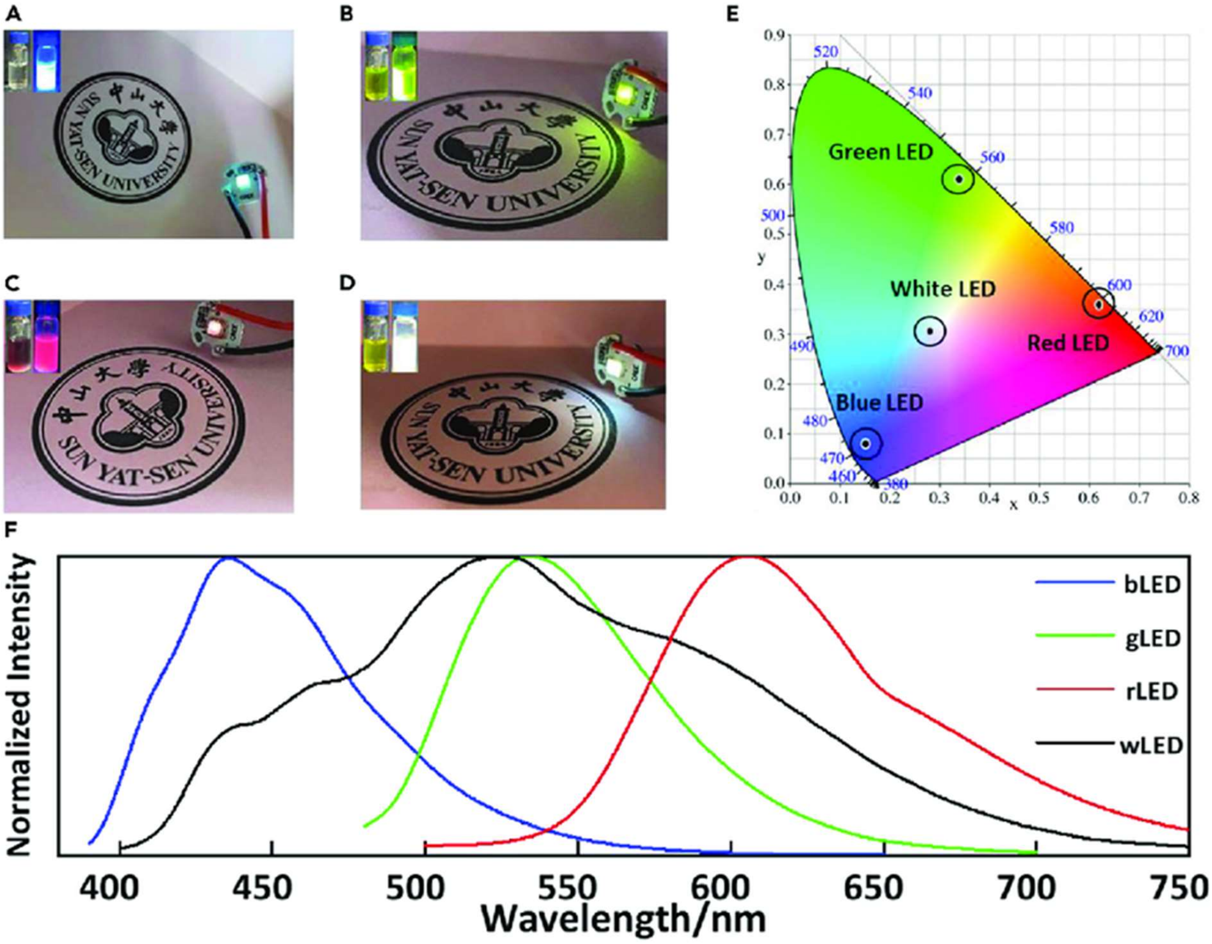

Figure 1. 9 Photos of full-color CQDs and its application in LEDs (A) Photo of d-bCQDs-based LED chip. (B) Photo of o-gCQDs-based LED chip. (C) Photo of p-rCQDs-based LED chip. (D) Photo of wCQDs-based LED chip. (E) CIE chromaticity coordinate of d-bCQDs, o-gCQDs, p-rCQDs, and wCQDs. (F) Emission spectra of the LEDs of d-bCQDs, o-gCQDs, p-rCQDs, and wCQDs (*iScience, 2022, 25, 104421*).

CQD-based LEDs have been used in a variety of applications such as displays, and lighting (Figure 1.9). CQDs embedded in a polymer matrix constitute flexible fluorescent materials that utilize the fluorescence of uniformly dispersed CQDs that do not exhibit solid-state quenching. These inexpensive films offer exceptional mechanical and thermal stability and can be used to create flexible solid-state lighting systems. CQDs have been utilized in a variety of functional layers, including electron-transporting layers, emissive layers, and hole-transporting layers, as well as an interlayer gap used to align and regulate the energy levels of other components in OLEDs[118]. CQDs have been used as the active material in **photovoltaics** due to their high absorption coefficient, high quantum yield, and tunable bandgap[119]. CQD-based photovoltaics have been used in a variety of applications such as solar cells, LEDs, and photodetectors. CQDs have been used in numerous types of **solar cells**, including dye-sensitized solar cells (DSSCs), organic solar cells (OSC), and silicon-based solar cells (Si- SC) [80]. In solar cells, CQDs have been used as active absorbing layers, electron-transporting layer (ETL), hole-transporting layer (HTL), donor/acceptor or dopant. Sofia Paulo and colleagues demonstrated the synthesis of CQDs and their use in solar cells [83]. **Bioimaging** is the process of visualizing and studying biological structures and processes, and CQDs have been explored as a potential material for bioimaging due to their unique optical and electronic properties[120]. CQDs have been used as vehicles for **drug delivery** due to their small size, high surface area, and biocompatibility[54]. CQDs can be functionalized with various molecules such as polyethylene glycol (PEG) to improve their stability and reduce toxicity. CQDs have been used as **photothermal agents** for cancer therapy due to their high absorption coefficient and ability to convert light energy into heat[121]. CQDs can be functionalized with various molecules such as antibodies or peptides to target specific cells or tissues. CQDs have been used as **biosensors** due to their high sensitivity and selectivity[44]. CQDs can be functionalized with various biomolecules such as enzymes or nucleic acids to detect specific biomolecules in biological samples. Semiconductor QDs such as CdSe and ZnS with a core-shell structure were also employed for in vivo and in vitro bio-imaging. Still, they showed the accumulation of metal ions in tissues and organs, leading to long-term cell death[122]. Compared to cytotoxicity and bioimaging, CQDs made by treating carbon soot with nitric acid and then heating it with PEG1500N to passivate it with oligomeric PEG were showed higher cell viability and used for bioimaging[123]. In addition to biocompatibility, the quantum yield percentage of CQDs is significantly higher, which makes them more luminous and non-blinking; for example, CQDs with QY of 20 percent at an excitation wavelength of 440 nm serves as the best bioimaging tools[123]. CQDs are superior options for in vivo imaging over QDs containing heavy metals due to their low toxicity. Under excitation, CQDs produced from various carbon sources and functionalized with the different functional groups may emit in the UV or NIR areas of the electromagnetic spectrum and can be utilized for in vivo imaging (Figure 1.10).

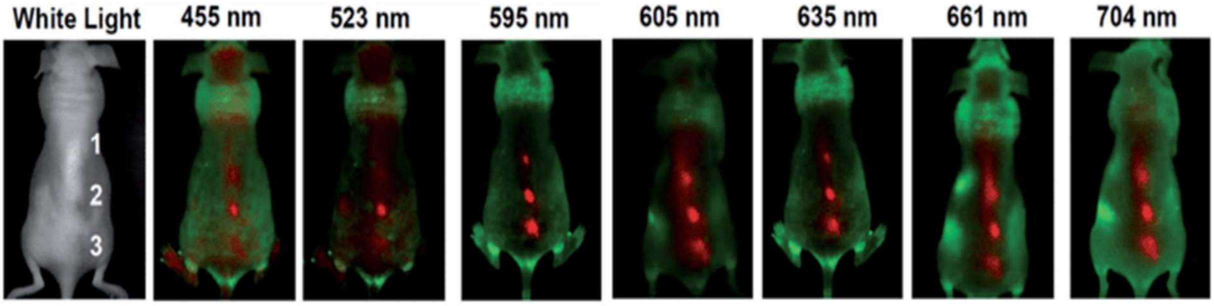

Figure 1. 10 CQDs-injected mice in vivo fluorescent images. Different excitation wavelengths were used. Red and green indicate CQD and tissue auto-fluorescence, respectively. (*RSC Advances 9(12):6460-6481*).

Lower levels of homogeneity in the CQDs samples make it feasible to separate brighter individual dots for improved optical characteristics. Longer wavelengths are chosen for in vivo optical imaging because photon-tissue penetration rises, and background auto-fluorescence diminishes[124]. The fluorescence emission intensity from most of the CQDs decreases at longer wavelengths; however, imaging at longer wavelengths reduces the auto-fluorescence coming from tissues, resulting in an enhanced signal-to-noise ratio. The CQDs were inject to an unclothed mouse in each of the three separate test sites. Figure 1.10 shows excitations at 595 nm and beyond produce images with superior signal-to-background separation, red spots were distinguished from the green background auto-fluorescence in the fluorescence images[125].

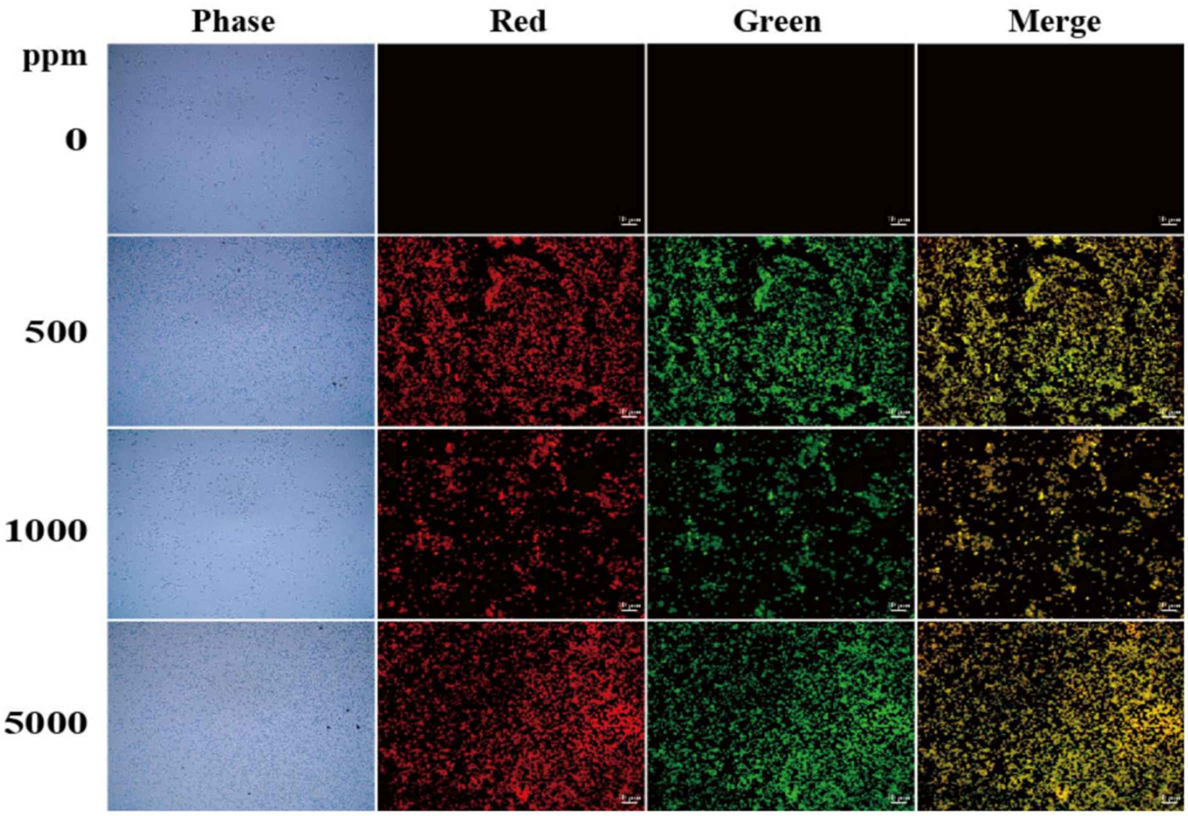

Figure 1. 11 Microscopic images of E. coli stained with N-CQDs at different concentrations of 0, 500, 1000, 5000ppm (*Crystals 2021, Vol. 11, Page 789, 11, 7, 7 2021*).

The cell membranes penetration (in vitro) of nitrogen-doped CQDs in E.coli has been shown in the at different concentrations ranging from 0 to 5000 ppm at a resolution of 10 µm, where red and green fluoresces were detected under the TRITC filter set and FITC filter set, respectively[126]. Due to its outstanding features like intense fluorescence, nano-dimensional size and consequent permeability to cell membranes leads, the potential application of CQDs has gained increasing interest in field drug loading and targeted drug delivery. A drug delivery application using CQDs is the delivery of anticancer drugs to cancer cells. In this application, CQDs are functionalized with antibodies that specifically bind to cancer cells. The functionalized CQDs are then loaded with an anticancer drug, and the CQD-drug conjugates are administered to the patient. The antibodies on the CQDs target the cancer cells and the anticancer drug is delivered specifically to the cancer cells, reducing the toxicity to healthy cells.For instance, Karthik et al. could covalently link 7-(3-bromopropoxy)-2-quinolylmethyl chlorambucil (Qucbl) to nitrogen-containing CQDs[127]. The spectroscopic techniques confirmed the addition of the medication on the outer surface of the CQDs. Further microscopic methods used for *in vitro* studies revealed that drug-loaded CQDs aggregated in the cytoplasm and nucleus. Several cancer drug molecules such as dopamine hydrochloride (DA), polyamine-containing organosilane and doxorubicin (DOX) were attached to CQDs to examine the in vitro release profile. The results suggest that drugs linked with CQDs have prolonged released time as long as 60h and high biocompatibility with Neur 2A cells compared to DA alone[128]. In addition to surface modification, several hollow CQDs were synthesized for drug loading. One current study shows that CQDs-DOX composites in the in vitro system are rapidly taken by the cells and exhibit pH-controlled drug release. A photothermal therapy application using CQDs is the treatment of cancer cells. In this application, CQDs are functionalized with antibodies that specifically bind to cancer cells. The functionalized CQDs are then added to a sample of cancer cells and irradiated with near-infrared (NIR) light. The CQDs absorb the NIR light energy and convert it into heat, causing damage or destruction of the cancer cells while minimizing damage to surrounding healthy cells. Another example is the treatment of bacterial infection by CQDs. CQDs are functionalized with specific peptides that target bacterial cells, and this functionalized CQDs are then added to a sample of bacterial cells. The sample is then irradiated with light, causing photothermal destruction of the bacterial cells. This method has been found to be effective in killing antibiotic-resistant bacteria, making it a promising alternative to traditional antibiotic treatments. PDT has several advantages over traditional ways of treating cancer, such as aggressive surgery, chemotherapy and radiotherapy. It is a non-invasive technique with high specificity where the targeted cells can be chosen correctly. Reports show that the CQDs have been used to stop the growth of the cancer cells MCF-7 and MDAMB-231[129]. CQD-based biosensors detect glucose, phosphate, nucleic acid, cellular iron, potassium iron, and pH. CQDs are a suitable fluorescent assay for identifying single-base mismatched nucleic acid. CQDs adsorb via π– π interactions to label a single-stranded DNA (ssDNA) probe, quenching fluorescence and hybridizing to its target to generate double-stranded DNA (dsDNA). Desorption of dsDNA from the CQD surface with greater recovered fluorescence probes the target DNA[130]. Reactive oxygen species (ROS) indicate cancer, DNA damage, infections or inflammations, arthritis, neurological problems, and chemotherapeutic drug screening. GLU is used as a biomarker in early-stage cancer diagnosis and many physiological conditions since it inhibits cancer cell proliferation and affects N-doped CQD fluorescence intensity[131]. Kong and his colleagues found that the terpyridine-based receptor molecule (TPY) covalently binds to CQD and changes fluorescence intensity due to H^+ ion adsorption-desorption. As the H^+ ion concentration increases, so does the CQD-TPY nano-emission probe's intensity in the 440–650 nm range[132].

CQDs are remarkable tools that offer both versatilities in manipulation techniques and usability. This field is worthy of investigation if further knowledge and application-based inventions are to be obtained.