

Chapter- 1

1 Introduction and Literature Review

Carbon is one of the most abundant substances on earth and can be found everywhere. Carbon is truly a remarkable element due to its distinctive and versatile properties compared to other materials. Carbon atoms can form single, double, and triple bonds due to the electronic configuration $1s^2 2s^2 2p^2$. It utilizes covalent contacts and weaker physical interactions like van der Waal forces, hydrophobic bonds, π - π and cation- π bonds. Carbon is able to hybridize its 2s and 2p atomic orbitals in three distinct ways: sp^3 (for single bonding, tetrahedral), sp^2 (for double bonding, trigonal planar), and sp^1 (for triple bonding, linear)[1]. Figure 1.1 shows Diamond, graphite, lonsdaleite, fullerene (C60, C70), amorphous carbon, carbon nanotubes, and graphene are allotropes of carbon[2]. Carbon is unusual among the elements in its ability to generate an extensive array of compounds. Carbon combines with hydrogen, oxygen, nitrogen, and other elements to make a huge number of compounds. Carbon atoms frequently bond to each other and make different types of compounds. For decades, carbon has been the topic of significant research attention.

1.1 Carbon Nanomaterials

Carbon materials are widely employed in nanoscale material science, ranging from zero (e.g. carbon dots, fullerene) to one (e.g. single-walled carbon nanotube) to two dimensions (such as graphene, graphene oxide)[3]. In the past two decades, carbon has been used as a potential non-toxic substitution in highly fluorescent quantum dots. Quantum dots typically have a

heavy metal core, resulting in inherent toxicity and complex preparation procedures but this new candidate have carbon core with some functional groups on surface which is known as carbon quantum dots (CQDs).

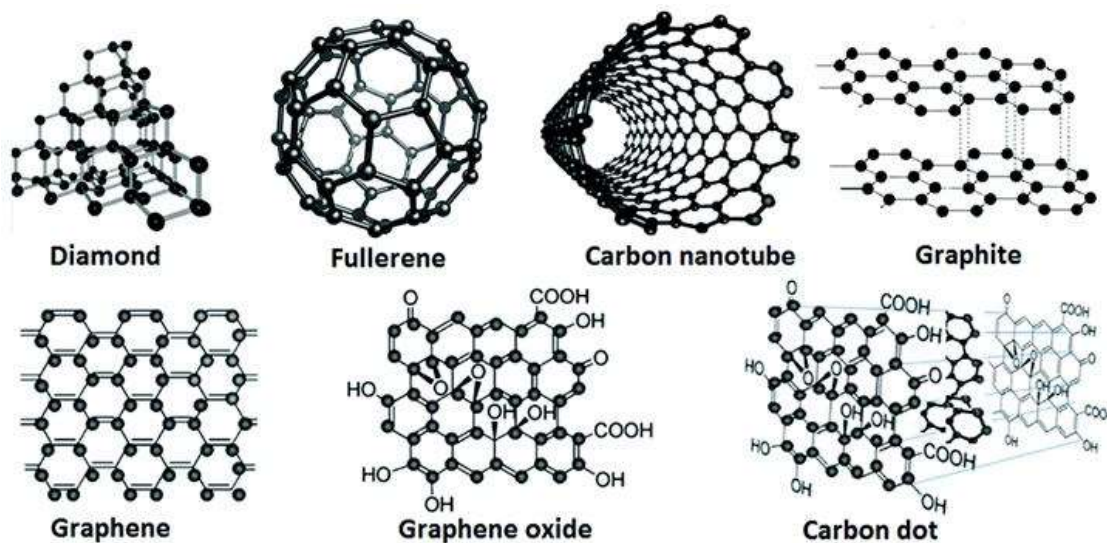


Figure 1.1 Allotropes of carbon nanomaterials (*Nanoscale*, 2016,8, 4799-4851)

1.1.1 Fullerene

The discovery of fullerenes in 1985 spawned a new field of study and a new class of pure carbon materials that are notably distinct from diamond and graphite. Kroto et al. at Rice University produced the spherical carbon molecules C₆₀ and C₇₀ by irradiating graphite discs in a helium jet using a laser[4]. These molecules are named fullerenes after the American architect Richard Buckminster Fullerene (1895-1983), who constructed the geodesic dome out of pentagons and hexagons. Fullerenes are a family of carbon-based compounds with a spherical, ellipsoidal, or cylindrical structure[5]. They are carbon atoms interconnected in pentagonal and hexagonal rings that form closed, hollow cages. Fullerenes with a spherical

shape are also known as bucky balls, whereas those with a cylindrical shape are known as carbon nanotubes or Bucky tubes[6]. Spherical fullerenes are zero-dimensional molecules since all dimensions are limited to the nanoscale. In order to develop new technologies based on the structural features of these nano-cages, particularly in the fields of electronics and biomedical engineering, intensive research was conducted. Spherical fullerenes have the chemical formula C_n , where n represents the number of atoms in the molecule. C_{60} , C_{70} , C_{76} , C_{80} , and C_{84} are among the isolated stable fullerenes, and the sequence extends to enormous fullerenes[7]. Fullerenes are chemically stable, but their dynamic stability is inferior to that of graphite. In order to create closed spheres, sp^2 -hybridized carbon atoms must be bent. Whereas in planar graphite, the atoms are at their lowest energy level.

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[8][9]. Geim and Novoselov has devised the rudimentary method for separating graphite into its constituent graphene sheets. This research group has demonstrated that single-layer graphene not only can be isolated from graphite sheets but they are also exceptionally stable at room temperature. Graphene is the two-dimensional (2D) carbon nanomaterials created by one or more graphite monolayers. Similar to the graphite structure, in graphene sheets the sp^2 -bonded carbon atoms are densely packed in a honeycomb crystal lattice with an average bond length of 0.142 nm[10]. A single layer of carbon atoms is referred to as a graphene sheet, whereas many sheets stacked with an inter-planar spacing of 0.335 nm are referred to as few-layer graphene. Graphene is the fundamental structural constituent of

other carbon-based nanomaterials, as it may be rolled into one-dimensional (1D) nanotubes or wrapped into zero-dimensional (0D) spherical fullerenes. In the free State, it was regarded to be unstable and non-existent. As a result of their tendency to roll and form scrolls to gain a lower energy state, it is challenging to obtain graphene layers that stand on their own. Many techniques have been devised for producing single-layer or few-layer graphene, including mechanical exfoliation, oxidation of graphite, liquid-phase exfoliation, chemical vapour deposition, thermal breakdown of silicon carbide, and nanotube cutting[11]. Graphene possesses several peculiar properties, such as the quantum Hall effect at ambient temperature, an ambipolar electric field effect, ballistic conduction of charge carriers, high elasticity, and a tunable band gap[12]. Due to its extraordinary physical and electronic properties, such as strong thermal conductivity, electron mobility, and specific surface are frequently utilized in contemporary industrial applications.

1.1.3 Carbon Nanotube

Iijima first discovered carbon nanotubes in 1991[13]. Carbon nanotubes (CNTs) are synthetic carbon allotropes distinguished by a network of sp^2 hybridized carbon atoms. There is only one dimension to this construction. Consideration is given to CNTs by rolling a two-dimensional graphene sheet into a cylinder with a hexagonal ring structure in the form of a tube, which may consist of single or several concentric layers of graphene (Figure 1.2)[14]. During synthesis, CNTs are capped by hemispheres of Fullerenes. CNTs offer exceptional mechanical, thermal, electrical, and optical capabilities that are being employed individually or in combination to produce sensitive sensors or multifunctional materials. Carbon nanotubes possess the highest aspect ratios and most amazing electrical and electronic properties present the biggest intellectual challenges and opportunities for creative applications[15].

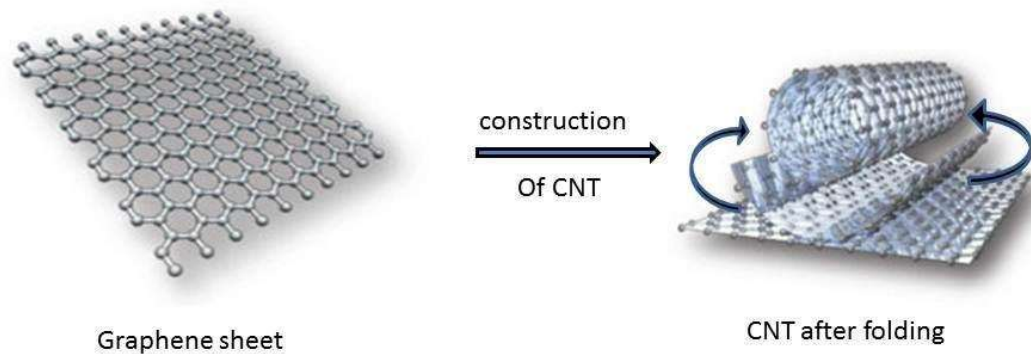


Figure 1.2 Graphene folding to make CNT (*Front. Syst. Neurosci.*, 8,91, 2014)

Typically, nanotubes are classified as either Single wall carbon nanotubes (SWCNTs) or multiwall carbon nanotubes (MWCNTs) as shown in Figure 1.3. SWCNTs are concentrically rolled up single layer of graphene sheet in the form of a cylinder with a diameter of approximately 0.7-3 nm, whereas MWCNTs comprise many concentric tubes having diameters of around 2 -25 nm and inter-layer distance of about 0.334 nm[16]. The lengths of both CNTs range from a few micrometers to centimeters, and their length-to-diameter ratios exceed 10,000. SWCNTs have drastically different physical properties than MWCNTs. Therefore precautions must be made while selecting the CNT type for specific applications. Theoretically, SWCNTs can form quickly, but in practically they are typical, and theoretically, MWCNTs can form easy, but in practically they are complex.

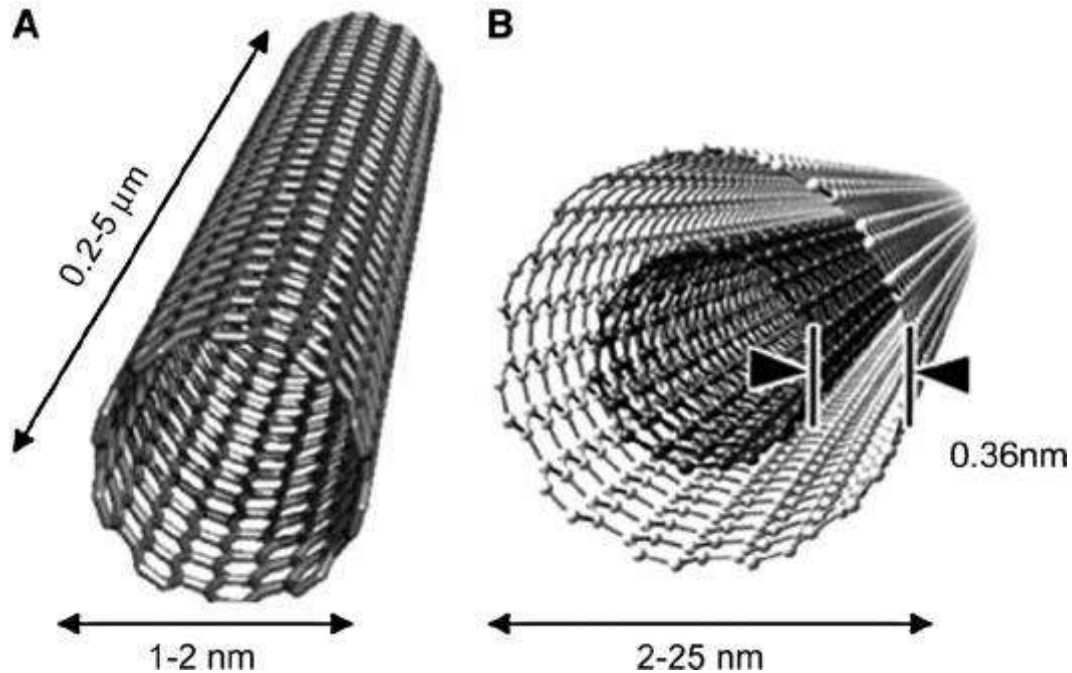


Figure 1.3 Structure of (a) SWCNT and (b) MWCNT (*Phys. Chem.*, 2013,109, 10-35)

A Graphene sheet can be rolled in multiple directions to form carbon nanotubes with metallic and semiconducting properties. Under the right conditions, three forms of carbon nanotubes are possible: armchair, zigzag, and chiral. Two parameters govern how a graphene sheet is folded: chirality or chiral vector 'C' and chiral angle 'θ'. To characterize such a fundamental property of the nanotube, it is possible to introduce two vectors, \mathbf{C}_h and \mathbf{T} (translational vector), whose rectangle forms the unit cell. \mathbf{C}_h is the circumferential vector on the tube's surface that joins two carbon atoms of same mass. $\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$ where \mathbf{a}_1 and \mathbf{a}_2 are the two graphite basis vectors and n and m are integers[17].

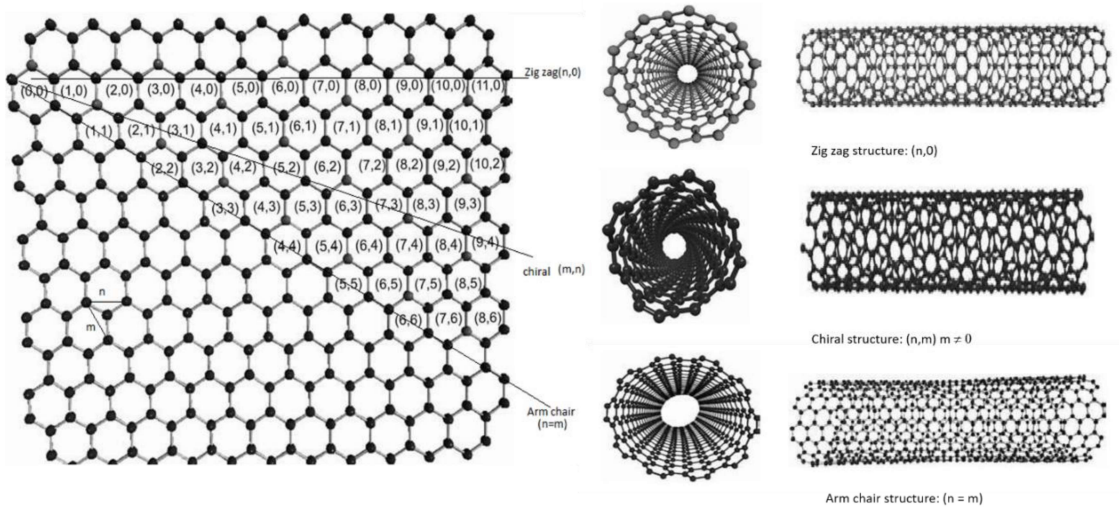


Figure 1.4 Single layered graphene sheet with integer labels (n, m). Types of CNTs knowing the numbers, the diameter and chiral angle may be determined (n, m) (*Nanoscale*, 2010, 2, 373-380)

Diameter, chiral angle, and type may be found using the integers (n, m) and the equation $\Theta = \tan^{-1}[\sqrt{3} n/(2m + n)]$ for the chiral angle. As indicated in the Figure 1.4 the chiral angle is utilized to divide carbon nanotubes into three classes distinguished by their electronic properties: armchair ($n = m$, $\Theta = 30^\circ$), zig-zag ($m = 0$, $n > 0$, $\Theta = 0^\circ$), and chiral ($0 < |m| < n$, $0 < \Theta < 30^\circ$). Metallic carbon nanotubes in armchairs (a degenerate semimetal with zero band gap)[18]. If $(n - m)/3 = I$ (I being an integer and $m \neq n$), zigzag and chiral nanotubes are semimetals with a finite band gap; otherwise, they are semiconductors. Whether a nanotube is semi-metallic or semi-conducting is determined by its band gap, which is inversely proportionate to the tube's diameter, giving each nanotube its electronic characteristics. The chiral angle and diameter of carbon nanotubes determine their electronic properties[19].

1.1.4 CNT Functionalization

In the synthesis process, pure CNTs are often heavily contaminated by metal catalysts and amorphous carbons[20]. The primary challenge in terms of technology is that they are insoluble in both water and organic mediums. Furthermore, they tend to congregate due to their extremely high van der Waals forces of attraction over long ranges, making their dispersion a challenging task[21]. It has been suggested that the surface functionalization of nanotubes may aid in resolving these problems. Functionalization often includes the attachment of substances to the sides or ends of CNTs, thereby enhancing their solubility and biocompatibility. Covalent or noncovalent bonding may be used to secure the extension[21]. For instance, the covalent attachment of a functional group to CNTs will yield stable functionalized CNTs, making these materials appropriate for various applications. Noncovalent functionalization offers the advantage of preserving the electronic structure of the atomic surface of nanotubes. Attaching polyethylene glycol (PEG) to the surface of carbon nanotubes increases their solubility. Adding PEG allows CNTs to be modified with terminal amine (PEG-NH₂) and carboxyl (PEG-COOH) groups, which provide biomolecule functionalization sites[20]. Biocompatibility is enhanced with PEGylated CNTs, and their use in medical implants is currently being studied[20]. Using a strong acid to treat CNTs is another frequent and systematic method for increasing solubility. This procedure eliminates metallic impurities from CNTs and creates COOH groups on their surfaces which enhance the solubility of these substances and provide a platform for the attachment of other chemicals[21]. Haddon group discovered SWNT functionalization using octadecylamine (ODA). The reaction is mainly an acid–base reaction in which ODA combines with carboxylic-functionalized SWNTs to create ODA-functionalized SWNT[22].

1.2 Carbon quantum dots

Carbon quantum dots (CQDs) was initially discovered in 2004 by "accident" via arc-discharging during the purification of SWCNTs[23][24]. CQDs are a kind of quasi-spherical nanoparticles typically spanning up to 10 nm. CQDs offer unique optical properties, such as highly fluorescence, stable and excitation dependent broad emission spectra, allow them to be utilised in a variety of applications like sensing, bio-imaging, catalysis, solar cell, and optoelectronic devices[25]. But most QDs were made from semiconducting materials, like cadmium and selenium, in organic-phase or water-phase systems. This has led to worries about toxicity and high cost[26]. In the last two decades, fluorescent CQDs, mainly consisting of carbon with some hydrogen, oxygen and nitrogen moieties, have garnered growing study attention due to their high biocompatibility, excellent optical property, low toxicity and resistance to photobleaching[27].

CQDs are often defined as a carbogenic core comprised of amorphous and crystalline sections with surface functional groups. Noticeably, although many researchers demonstrated the existence of a crystalline sp^2 carbon section, CQDs possess poorer crystallinity, namely with more defects than Graphene QDs, which usually have graphene lattices inside the dots resembling the crystalline structure of single or few-layered graphene[28]. These minuscule sp^2/sp^3 carbonaceous cores often possess oxygen and nitrogen-containing or changed functional groups on their surface to produce defects. Many structural models of the CQD core have been suggested, such as diamond-like structure, graphite/graphite oxide structure, and amorphous carbon structure, while the majority of them have a graphitic structure[29]. CQDs are environmentally friendly, highly biocompatible, and chemically inert and they exhibit excellent water solubility, dispersibility, and stability[30].

1.2.1 Synthesis Methods of CQDs

Typically, the order of events that follow CQDs formation is dehydration, condensation, polymerization, carbonization and passivation. Depending on the synthesis techniques, precursor materials and thermodynamic conditions, carbonization may be inadequate, resulting in amorphous structures like polymer chains and functional groups inside the produced quantum dots[31]. The synthesis methods of CQDs can generally be categorized as "top-down" or "bottom-up" (Figure 1.5). The former entails decomposing carbonaceous materials through chemical, electrochemical, or physical means. This method is carried out via pyrolysis or carbonization of small organic molecules or by step-by-step chemical fusion of small aromatic molecules[32].

Using **top-down approach**, the bulk material is reduced to a very fine particle in order to create nanoscale materials, specifically quantum dots. The majority of these processes, which include arc discharge, laser ablation, electrochemical approach, and ultrasonic treatment, involve the chemical or mechanical disruption of non-fluorescent macroscopic carbon materials into nano-sized photo luminescent CQDs[33]. In the **arc discharge process**, a direct-current arc voltage is delivered across two graphite electrodes bathed in an inert atmosphere, and crude carbon nanotube soot is converted into CQDs[34]. Xu and co-workers discovered CQDs in 2004 during the purification of SWNTs via an oxidation procedure involving nitric acid in the arc discharged soot. The developed CQDs exhibited robust photoluminescence at 400 nm excitation wavelength. In 2011, Hu et al. used a pulsed laser to irradiate graphite flakes mixed in PEG solution for four hours with ultra-sonication, producing a homogenous black suspension[35]. After centrifugation, CQDs were recovered from the coloured supernatant. CQDs can also be produced using an **electrochemical method**. Yao and colleagues (2014)

described the electrochemical production of blue fluorescent CQDs with a size of 2-3 nm in pure water. In an aqueous solution, the resulting CQDs exhibited good fluorescence and thermodynamic stability[36]. In addition, the energy of ultrasonic waves can be employed to transform macroscopically sized carbon materials into nanoscale CQDs. Ma et al. (2012) have developed a straightforward ultrasonic method for the synthesis of nitrogen-doped CQDs (N-CQDs) using aqua ammonia and glucose as precursors[37]. The produced N-CQDs exhibit excellent dispersibility in water, high stability, and strong PL performance when excited by visible light.

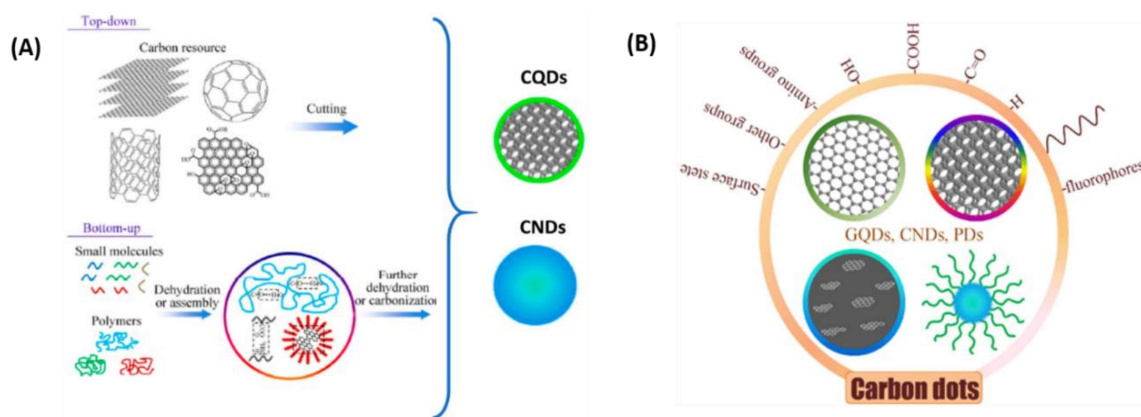


Figure 1.5 (A) Top-down and bottom-up approaches; CQDs represents crystalline carbon quantum dots while CNDs represent disordered carbon nanodots. (B) Typical structure of CQDs where core can be crystalline or amorphous and surface is decorated with functional groups. (C – *Journal of Carbon Research* 5(4):60, *NanoResearch*,12274, 2014)

In the **bottom-up approach**, precursors serve as small molecules and produce nanoscale materials under various reaction conditions, most frequently heating or microwave [38]. Hydrothermal/solvothermal synthesis, microwave-assisted method, and template method are the principal bottom-up techniques for CQDs preparation. In hydrothermal/solvothermal synthesis, small organic molecules undergo condensation, polymerization, carbonization, and

passivation to produce CQDs in water or an organic solvent at high temperatures and pressure[39]. By modifying and choosing appropriate reaction temperature, duration, solvents, and raw materials, it is simple to regulate the optical characteristics of CQDs. Additionally, this strategy aids in obtaining a comparatively greater quantum yield (QY) than in previous ways. The hydrothermal technique is now the most popular approach for synthesizing CQDs due to its non-toxicity, low cost, and straightforward operation. The bottom-up methods have apparent advantages over the top-down strategy when selecting diverse organic precursors and accurately managing morphology and size distribution; hence, it is utilized more frequently in synthesizing of CQDs[40].

1.2.2 Hydrothermal Process

CQDs have been produced through the hydrothermal method using Teflon lined autoclave and an oven. This method involves heating carbon compounds at a high temperature and pressure, hence forcing precursor molecules to interact with water molecules. When heat was applied to a mixture, the pressure rose, which resulted in the deoxygenation of the water molecules. Carbon layers were repelled due to the production of H^+ and OH^- ions. However, the high-pressure condition can be managed by utilizing a Teflon walled stainless steel autoclave. Self-assembly can be used to make CQDs by oxidizing carbon sheets to generate additional oxygen-containing functional groups. During the process, the size of CQDs was reduced, resulting in high fluorescence emission. The hydrothermal process can yield a substantial amount of quantum dots with homogenous particle size distribution. High production yields are significant because they can help improve the photo luminescent characteristics of CQDs through greater surface passivation.

A study produced fluorescent CQDs with an average size of around 1.7 nm and a yield of 38.6 percent from gelatin. In Teflon lined autoclave, gelatin was dissolved in water and synthesized for three hours at 200°C[41]. Moreover, broccoli was utilized in the hydrothermal synthesis of CQDs. Throughout this procedure, heat energy was maintained within the broccoli juice to ensure complete conversion of the broccoli juice to the CQDs solution. The reactor was placed in a 190 °C oven for six hours. A solution of dark brown CQDs can be used to detect silver ions[42]. In another study, CQDs were synthesized through the hydrothermal technique utilizing Lemon juice in a solution of ethanol at 120 °C for three hours. The product was then dialyzed for 24 hours to eliminate contaminants[43].

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

Biomass	Q.Y.	PL	Application	Ref.
waste milk		Blue	chromium-ion sensing and supercapacitor applications	[44]
Coriander	6.48	Blue	Antioxidants, bio-imaging	[45]
Chitosan	13	Blue	Nitro aromatics detection	[46]
Watermelon	7.1	Blue	Optical imaging probe	[47]
Tamarind leaves	46.6	Blue	Mercury detection	[48]
Sweet lemon		Green	Gene therapy and breast cancer detection	[49]
citric acid and 2,3-dionaphthalene	70	Green	Dye sensitized solar cell	[50]
Grass		Green	Removing water pollutants	[51]
Pineapple peel	0.42	Blue	Sensor, memory devices, mercury detection	[52]
Rice residue and glycine	23.48		Heavy metal detection	[53]

Microwave techniques have also attracted the interest of researchers as a method for synthesizing CQDs. Microwaves with homogenous energy are frequently used in the synthesis of CQDs due to their superiority in terms of speed, efficiency, and practicality. Zhu and his colleagues initially produced fluorescent CQDs with a limited size distribution by pyrolyzing polyethylene glycol and saccharide in the presence of high frequency microwave radiation[54]. Reza et al. synthesized CDs by heating a solution comprising citric acid, urea and thiourea in a home 450 W microwave at 5 minutes for the detection of mercury and iodine[55].

Surface Modification of CQDs: Chemical and physical alterations to CQDs are anticipated to enhance their photo-physical properties, resulting in improved performance in various applications. Usually, these modifications are based on distinct criteria that support various CQD implementations. Its compositions and structures include a great deal of uncertainty. The existing modification schemes, such as surface functionalization, core-shell architecture, heteroatom doping, and composite material blending were reported in many recent publications[56]. 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[57]. 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[58]. Hydrothermally produced NCQDs from chitosan. When ethanol precipitation was employed to purify, 85.3% product yield was achieved[59].

1.2.3 Properties of CQDs

UV- Absorption property: The optical characteristics of CQDs play a significant role in determining their absorption and fluorescent property. The UV–vis absorption spectra of the CQDs range from 220 to 320 nm, with a visible-range tail. Molecular orbital (MO) theory can be utilised to illustrate the electronic structures of CQDs. In most cases, CQDs exhibit n- π^* and π - π^* transitions due to their conveniently accessible transition energies[60]. 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[58].

Photoluminescence property: Fluorescence is the emission of light by a substance that absorbs light with a shorter wavelength (more energy) and emits light with a longer wavelength (lower energy). After a few hundred nanoseconds, fluorescence disappears upon removal of the light source[61]. Fluorescence quantum yield (QY) is the ratio between the number of emitted and absorbed intensities, while fluorescence lifetime is the average time a fluorophore spends in an excited state before emitting photons[62]. Thus, the development of eco-friendly fluorescent CQDs with high quantum yield and long fluorescence lifespan is highly desirable for various practical applications. Several mechanisms have been proposed over the years, including quantum confinement effect, surface states or defects, molecular states and crosslinked enhanced molecular effect, to explain the PL of the CQDs and a unanimous method is yet to be decided. Due to the quantum confinement phenomena, the luminescence of CQDs can be adjusted in relation to their sizes by controlling the amount of energy levels an electron

can occupy. The exciton Bohr radius is the average distance between an electron and a hole in a bulk semiconductor. When the size is reduced below the exciton Bohr radius, the bandgap increases and the electron energy levels separate[63]. Consequently, CQDs with a fixed chemical composition can emit fluorescence at different wavelengths if their sizes differ as shown in Figure 1.6.

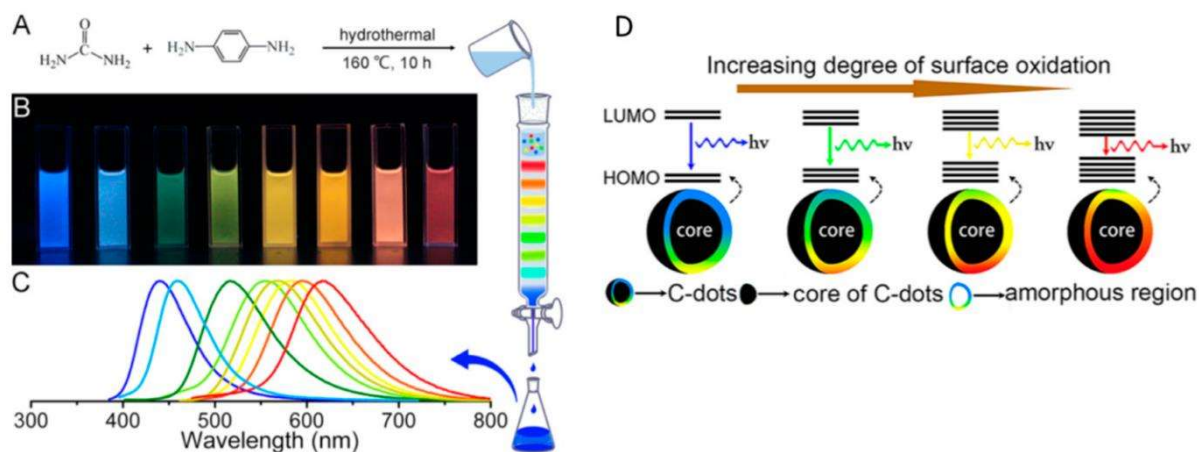


Figure 1.6 (A) synthesis and purification of CQDs (B) CQDs samples under UV-light (365 nm), (C) PL spectra at different wavelength, and (D) Tunable emission spectra of CQDs with different degree of oxidation. (*ACS Nano* 2016, 10, 1, 484–491)

The surface state of a CQDs is made up of the functional groups on the carbon dots and any surface defects. When a photon is absorbed, the HOMO electrons move to the LUMO energy band. This process is followed by the vibrational relaxation process, which does not release energy. Vibrational relaxation is the process by which the energy in electrons is lost by converting it to kinetic energy in other vibrational modes. It is a quick change, and electrons don't usually move up or down in the core electronic level. After the electrons' vibrations slow down, they release energy as photons and return to the HOMO energy level. This phenomenon is called fluorescence, and it takes about 10^{-9} to 10^{-7} seconds for it to happen. Most of the time,

the surface of a carbon dot has a lot of oxygen functional groups like -COOH, -C=O, and -C-O-C, as well as other nitrogen and sulphur groups from the precursor material and the synthesis routes[31]. 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[64]. The bandgap of CQDs changes when there are surface states, which changes the fluorescence properties. Controlled functionalization was one of the most common ways to get a wide range of fluorescence emissions from CQDs.

In recent years, research on the photoluminescence (PL) of CQDs has expanded significantly. PL is one of the most exciting properties of CQDs, and it has been used in photocatalysis. PL emission is like Stokes emission in that the wavelength of the PL emission is longer than the wavelength of the excitation[28]. In the scientific literature, many reports of PL emissions in CQDs have been put down to many different things. When you look closely at the spectral properties of the emissions and the structural properties of the materials they come from, you can see that most of the reported PL emissions can be roughly put into two types. The first is caused by bandgap transitions in conjugated π -domains, while the second is caused by defects in the structures of graphene and has a more complicated origin[65]. Since making or causing π -domains often depends on taking advantage of or manipulating flaws in graphene sheets, the two groups are often linked. Many studies have examined how PL emission and the excitation-wavelength (λ) of CQDs are related. Sun et al. say that fluorescent CQDs treated with polyethylene glycol (PEG1500N) or propionyl ethyleneimine-co-ethyleneimine (PPEI-EI) emissions are broad and dependent on the excitation wavelength[66]. Figure 1.7 shows the tunable emissions of surface-passivated C-dots may emerge from the varying fluorescence

properties of particles of different sizes and the distribution of distinct emissive sites on the CQDs surface.

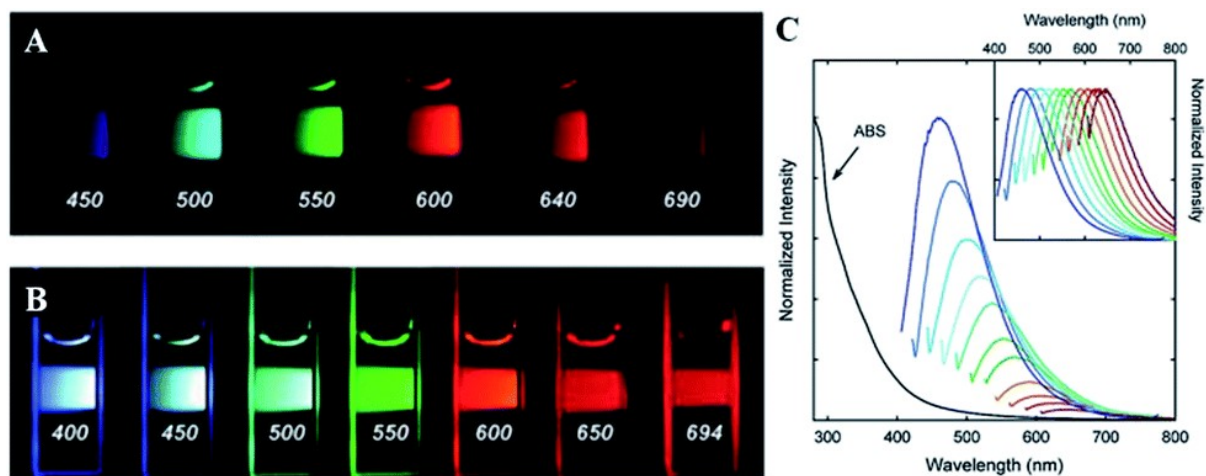


Figure 1.7 Photograph of polyethylene glycol of CQDs excitation wavelength at 400 nm and Absorbance and PL spectra. (*J. Am. Chem. Soc.* 2006, 128, 24, 7756–7757)

Chemiluminescence property: Since CQDs are exceptionally good electron donors and acceptors, they have been popularly harnessed for their chemiluminescence (CL) and electrochemiluminescence (ECL) for applications in catalysis, sensing and optoelectronics. By injecting oxidants, holes can be injected into the CQD surface, significantly improving energy release in the form of ECL emission by electron-hole annihilation[67]. The dual ability of CQDs to operate as both electron donor and acceptor offers tremendous potential for their usage in optoelectronics, catalysis and sensing. Recently, phosphorescence was seen in CQDs produced by limiting their rotational and vibrational mobility in a hard matrix.

Up-conversion photoluminescence (UCPL): Up-conversion fluorescence exhibits anti-Stokes behaviour, wherein a longer excitation wavelength results in a shorter emission wavelength. Most CQDs do not exhibit UCPL, and the observed peak may imply a typical

fluorescence peak stimulated by some leaky component from the excitation of second-order diffraction light in the monochromator of the fluorescence spectrophotometer[68]. These factors can be eliminated by adding a suitable long-pass filter in the excitation pathway before deducing UCPL. Another exciting element of CQDs that is being researched is the **photo-induced electron transfer property (PET)**. CQDs have been examined for photo-response, electron transfer and photo-induced charge separation processes as they have an active electron accepting/ donating surface. Such efforts are bound to advance the existing mechanistic understanding and many applications in catalysis and related light-energy conversion reactions.

1.2.4 Application of CQDs

CQDs offer strong biocompatibility, low toxicity, and unique optical properties, such as high fluorescence stability, broad excitation and emission spectra, which enable them to be used in applications of sensing, bio-imaging, catalysis, solar, and optoelectronic devices (Figure 1.8). Therefore, the following sections will examine the application of CQDs in numerous fields.

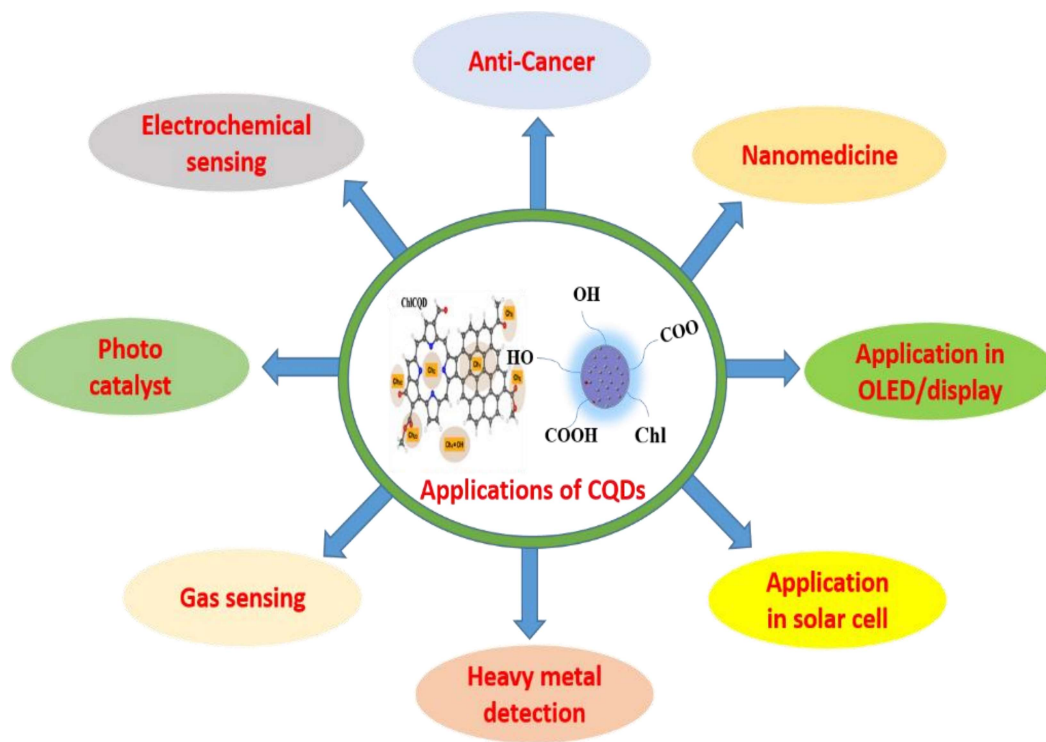


Figure 1.8 Various applications of carbon quantum dots.

Chemical Sensing Application: Physical and chemical properties of an analyte are converted into a measurable signal by a chemical sensor. Typically, the intensity of the observable signal is proportional to the analyte concentration. Chemical sensors have two major detection modes, photochemical and photometric, and they are used to determine the concentration or variations in chemical processes with the highest degree of precision. Research work included in this thesis examines the synthesis of CQDs from green precursors for the detection of diverse analytes in drinking water, including chemical contaminants, heavy metal ions and also biologically active small molecules. Various environmental synthesis techniques of CQDs, together with their benefits and drawbacks, are also described. The interaction of functional CQDs with analytes causes subsequent variations in fluorescence turn-on (enhancement) or

turn-off (quenching) in the CQDs[69]. The fundamental principles of CQD sensors have been explained using detection processes such as photo-induced electron transfer (PET), fluorescence resonance electron transfer (FRET), aggregation-induced red-shift emission (AIRSE), and inner filter effect (IFE). CQDs have been used to develop precise sensors for metal ions with detection limits in the micromolar, nanomolar, and even picomolar ranges. However, as unique fluorescence sensors, CQDs offer inherent simplicity, high sensitivity and selectivity, low cost, and minimal instrumentation requirements.

The existence of functional groups includes carboxyl, hydroxyl, and amino on the surface of CQDs. The outer layer of CQDs interacts efficiently with metal ions via surface bonding, hence allowing for the change in CQD characteristics. In addition to metal ion sensing, it has been claimed that detecting biomolecules is a growing use of CQDs. Yang et al. (2019) studied L-cysteine detection with Red- emissive CQDs and Fe^{3+} . The addition of Fe^{3+} ions suppressed the intense fluorescence of R-CDs, which was subsequently restored by the addition of L-cysteine. Due to the strong interaction between L-cysteine and Fe^{3+} , this R-CDs/ Fe^{3+} combination exhibited outstanding selectivity and sensitivity, with a LOD of $0.27 \mu\text{M}$ [70]. Zhou et al. reported in 2018 that haemoglobin could be found using a fluorescent nano-biosensor made of molecularly imprinted polymers and CQDs to turn off the fluorescence. The manufactured biosensor displayed an exceptionally low LOD (0.77 nM) for hemoglobin, along with great sensitivity and selectivity[71]. Recent advances in the use of green CQDs to detect heavy metal ions such as Aluminium (Al^{3+}), Arsenic (As^{3+}), Cadmium (Cd^{2+}), Chromium (Cr^{4+}), Copper (Cu^{2+}), Cobalt (Co^{2+}), Gold (Au^{3+}), Iron (Fe^{3+}), Lead (Pb^{2+}), Mercury (Hg^{2+}), Silver (Ag^+) and Zinc (Zn^{2+}) are examined in depth, as are their sensing methods[53]. We anticipate that our literature evaluation will help the future implementation of biocompatible

CQDs that use optical characteristics to detect heavy metal contamination (Figure 1.9). Numerous plant-derived CQDs have been used to detect metal ions in water, including Lotus root for Hg^{2+} and cell imaging[72], Strawberry for Hg^{2+} [73], Bamboo leaves for Pb^{2+} and Hg^{2+} [74], Jackfruit seeds for Au^{3+} [75], Papaya for Fe^{3+} [76], Mung bean for detecting Fe^{3+} [77], and Tulsi leaves for Cr^{4+} detection[78].

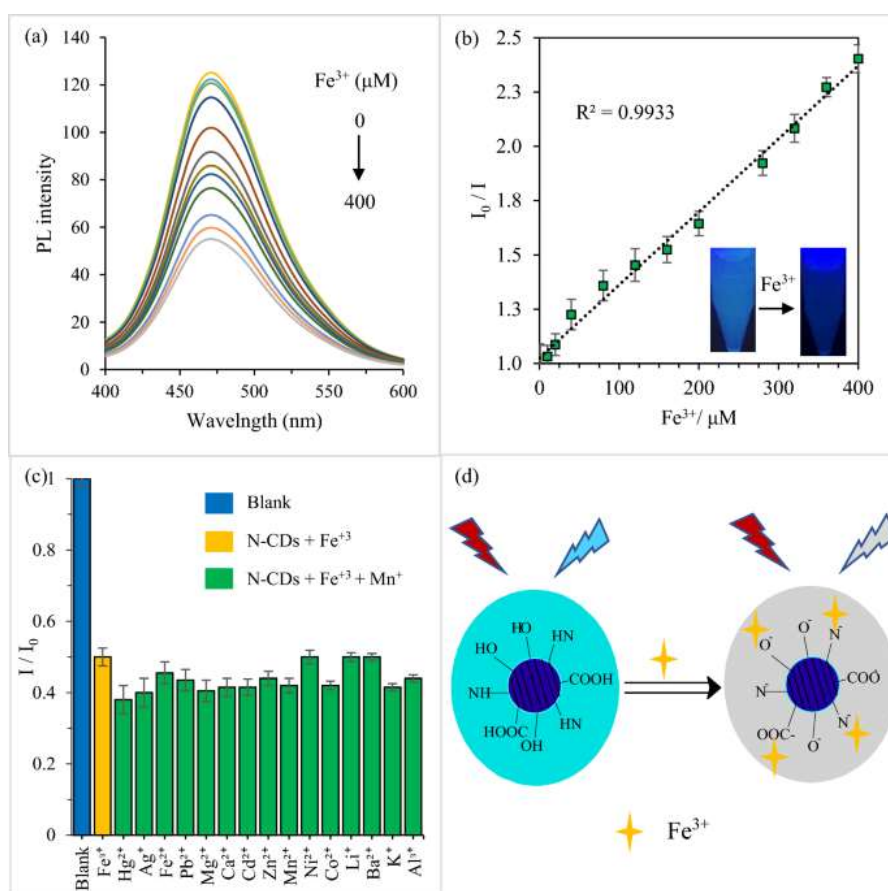


Figure 1.9 (a) N-CQDs based fluorescence quenching Fe^{3+} detection, (b) Conc. Dependent linearly fitted curve, (c) selectivity with Fe^{3+} and (d) schematic representation of Fe^{3+} detection mechanism. (*Scientific Reports*, 10, 11710, 2020)

Optoelectronic Application: CQDs have enormous potential for use in optoelectronic applications such as light-emitting diodes, laser diodes, photovoltaic solar cells, and photodetectors due to their large surface-to-volume ratio and unique optoelectronic properties. CQDs possess high electron and hole mobility, rapid electron extraction, adjustable bandgaps, and strong steady fluorescence[79][80]. Due to their simplicity of synthesis, inexpensive manufacture, eco-friendly and non-toxic nature, and stable, strong long-range fluorescence, CQDs have found widespread use in **light-emitting diode (LED)**-based applications. 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[81]. Typically, in LED the emissive layer of CQD is placed between the electron and hole transport layers. Figure 1.10 shows the same CQDs can be used to tune fluorescence emission to white, blue, cyan, or magenta by altering the voltage/current[82].

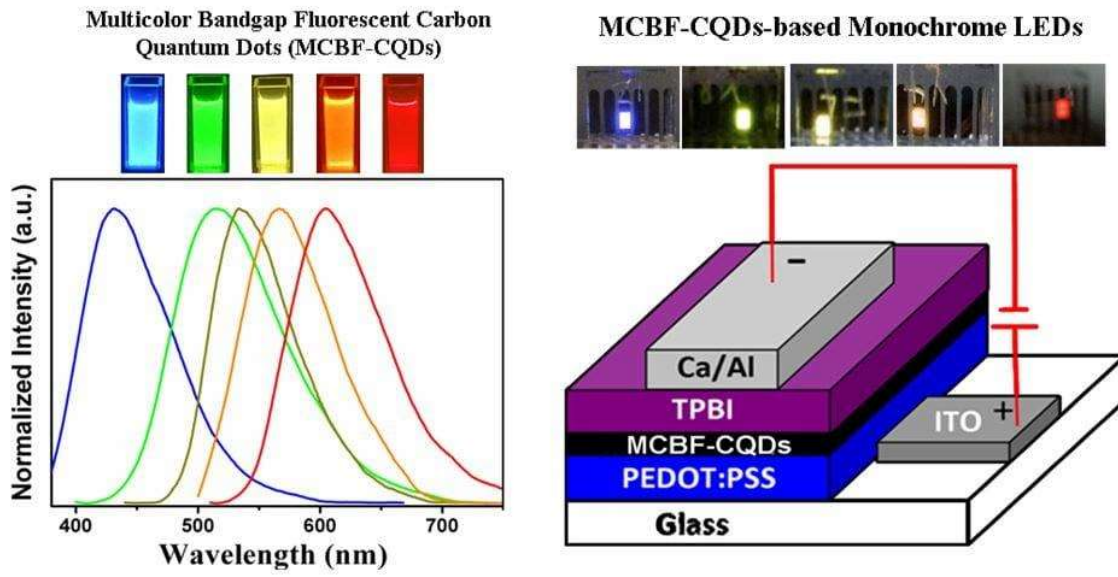


Figure 1.10 Multicolored size dependent carbon dots, Device structure and electroluminescent spectra of light-emitting diode (LED) (*Advanced Materials*, Volume 29, Issue 3 1604436)

CQDs typically exhibit a broad spectrum of light absorption extending into the visible area, which is advantageous for their use in **solar cells**. CQDs have been utilized in numerous types of solar cells, including dye-sensitized solar cells (DSSC), organic solar cells (OSC), and silicon-based solar cells (Si-SC)[80]. Sofia Paulo and colleagues demonstrated the synthesis of CQDs and their use in solar cells[83]. Using the hydrothermal technique, citric acid and p-phenylenediamine were completely dissolved in DI water and heated at 200 °C for five hours. After the reaction, a brown-black solution containing CQDs as hole transport material in perovskite solar cells was formed[83]. This form of solar cell is currently a hot issue in photovoltaic research due to its exceptional power conversion efficiency.

Supercapacitors are another application of CQDs that has gained interest. CQDs with porous surfaces can be used as electrode materials to improve supercapacitor performance. Moreover, CQDs support a higher surface infiltration rate than other materials, which can facilitate

electrode-electrolyte interactions, enhancing capacitive polarisation and favourably influencing capacitance levels[84].

Biomedical Application: The unique optical properties, photochemical stability, and catalytic properties of CQDs make them suitable for various biomedical applications. CQDs with biocompatibility, high hydrophilicity and water solubility are frequently used for *in vitro* and *in vivo* applications. The excitation-dependent fluorescence emission and high photo-stability provide additional advantages for fabricating bio-imaging tools and targeted drug delivery carriers. In the last few years, CQDs have been employed in various biomedical applications such as bio-sensing, bio-imaging, drug delivery, gene therapy, Photodynamic therapy (PDT) and cancer treatment. The presence of an active functional group on the outer surface also provides the binding sites for other tiny atoms and biomolecules such as antibodies, metal ions, peptides to target cancer cells and molecular biomarkers using optical and physical techniques[63]. Several studies have reported the performance of CQDs and CQDs functionalized nanoparticles for bio-imaging. CQDs are chosen over conventional organic dyes and fluorescent proteins due to several advantages. Most of the traditional dyes show photo-bleaching over repetitive exposure with significant toxicity at higher concentrations. However, CQDs resist photo-bleaching and metabolic degradation and show remarkable biocompatibility at higher concentrations without fluorescence quenching[85].

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[86]. 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[87]. 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[87]. 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.

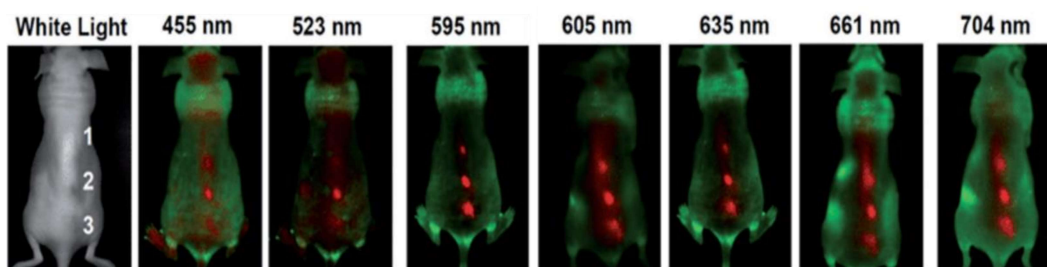


Figure 1.11 CQDs-injected mice in vivo fluorescent images. Different excitation wavelengths were used. Red and green indicate CQD and tissue auto-fluorescence, respectively. (*RSC Advances* 9(12):6460-6481)

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[88]. 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 injected to an unclothed mouse in each of the three separate test sites. Figure 1.11 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[63]. The cell membranes penetration (in vitro) of nitrogen-doped CQDs in E.coli (Figure 1.12) 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[89]. 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.

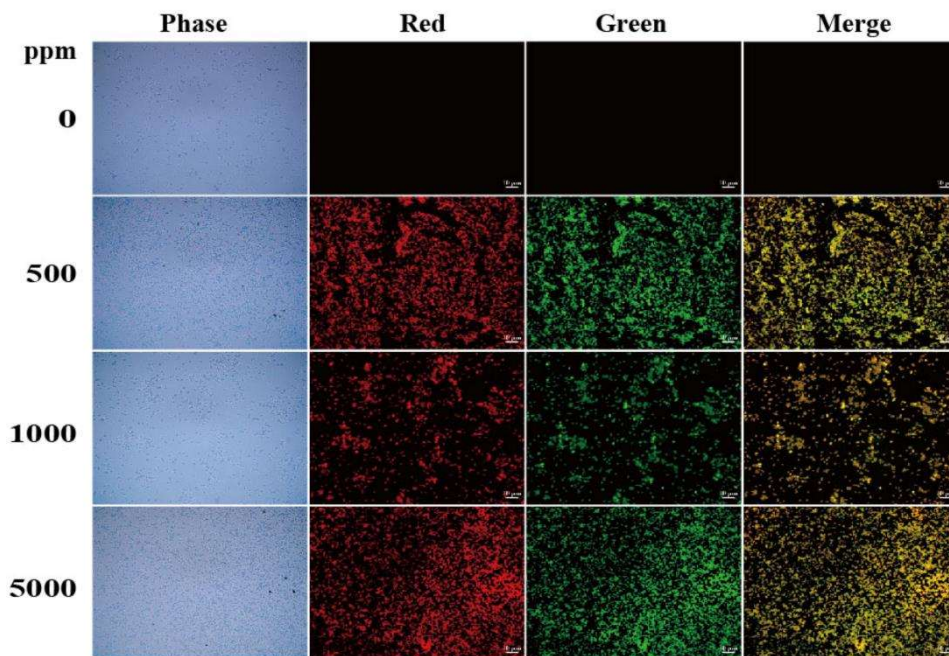


Figure 1.12 Microscopic images of E.coli stained with N-CQDs at different concentrations of 0, 500, 1000, 5000ppm (Crystals 2021, Vol. 11, Page 789, 11, 7, 7 2021)

Drug Delivery: Recently, several studies have shown the injection of CQDs in vivo and in vitro models for monitoring drug release for targeted drug delivery. For instance, Karthik et al. could covalently link 7-(3-bromopropoxy)-2-quinolylmethyl chlorambucil (Qucbl) to nitrogen-containing CQDs[90]. 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[91]. 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. The fluorescence emission from the CQDs helps to identify the sites of drug release and absorbance of the drug using fluorescence microscopy. Another study confirms that the CQDs-DOX had been absorbed by the A549 cells and were primarily located in the cytoplasm[92]. Passivated composites of CQDs were designed with the addition of polyamine-containing organosilane molecules to deliver DOX in the cytoplasm and the nucleus. Organophilic CQDs were used to deliver the anti-cancer drug curcumin in HeLa cells with high loading efficiency and rapid penetration[93].

Photodynamic Therapy (PDT): CQDs are a potential candidate for PDT treatment, which is used to kill superficial tumors turned on by laser light. CQDs are promising photosensitizers because they can generate reactive oxygen species (ROS) via light absorption and utilizing widely for cancer treatment[94]. 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[95].

Bio-sensing: CQDs are used as biosensor material due to their optical, chemical and electronic properties. The intense fluorescence emitted by CQDs has been used to fabricate fluorometric sensors for detecting a wide range of molecules. The chemical functionality and electronic properties helped to design voltammetric and optical sensors. The physical properties of CQDs, such as water solubility, high reactive surface area, wavelength-dependent multi-color emission, permeability to cells, and robust photo-stability, helps to fabricate a plethora of devices based on different sensing mechanism. 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[96]. 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[97]. 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[98].

Catalytic Application: CQDs can be used as efficient catalysts for the click reaction, photo-oxidation, ring-opening, aldol condensation, etc. CQDs control and boost the catalytic activity of other nanostructures due to active sites leading to the rapid electron transfer between the

host and donor molecules. In recent reports, CQDs are frequently used for Photocatalysis, peroxidase-like catalysis, electro-catalysis, Fenton-like catalysis, and chemical catalysis[99]. Photocatalysts have been seen as optimistic materials for application in clean energy and the treatment of contaminants. Photocatalysis is a catalytic reaction where a catalyst absorbs light. Novel materials with lower band gaps are needed to increase visible light absorption. Traditional photocatalysts like TiO_2 , BiPO_4 , Bi_2O_3 , and BiO_x ($X = \text{Cl, I, Br}$) have weak light absorption, a broad bandgap, and fast charge recombination[99]. CQD-based composite photocatalysts can increase light utilization efficiency and photocatalytic performance because CQDs' conjugated π -structure can promote photogenerated charge transfer and operate as electron acceptors following photoexcitation. CQDs-based composite photocatalysts are commonly utilized to photodegrade organic pollutants with a 90% efficiency. CQDs have a large light absorption area and abundant surface functional groups. Photocatalysis can occur under solar light due to CDs broad light absorption spectrum.

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.