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**CHAPTER 1**

**Introduction and Literature Survey**

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## 1.1 Introduction

The term ‘nano’ is referred to Greek prefix which means ‘dwarf’ or something extremely small and describes one thousand millionth of a meter ( $10^{-9}$  m). The concept of “nanotechnology” was introduced by American physicist and noble laureate Richard P. Feynman during the annual conference of the American physical society in 1959 at the California institute of technology (Caltech). He offered a speech entitled “There is a Plenty of Room at the Bottom” and described the world in which atoms could be influenced at an extremely small scale i.e. the nanoscale [Feynman (1960)]. He is known as the father of modern nanotechnology. Fifteen years later i.e. in 1974, the term nanotechnology was first of all used and defined by a Japanese Professor, Norio Taniguchi. According to him, nanotechnology is the process of partition, consolidation, and deformation of material by one atom or one molecule. [Taniguchi (1974), Handy *et al.* (2008) ]. Nanotechnology is a type of molecular engineering that assures many societal settlement, as well as improvement in health behavior and medical analysis, quicker and cheaper material, more proficient energy source, and electronic products. The most primitive, extensive explanation of nanotechnology refers to the challenging scientific objective of specifically manipulating atoms and molecules for the production of macro scale products, as well currently known molecular nanotechnology. A more widespread explanation of nanotechnology was consequently established by the National Nanotechnology Initiative (NNI) in the united state, which defines nanotechnology as a science, technology, and engineering performed at the nanoscale (1-100 nm) and manipulating materials by using these technologies are known as nanomaterials. In recent times, the nanomaterials are getting enormous attention of researchers engaged in the field of physics, chemistry, and biology to engineering, electronics and medicine, such as catalysis, energy, optics, science, chemical industries, space industries,

stain-resistant clothing, environment, pesticides, cosmetics, paints, sunscreens, automotive, biomedical, drug-gene delivery, health care, sporting goods, mechanics, nonlinear optical devices, light emitters, single electron transistors, diodes, digital cameras, and photo-electrochemical applications. The important characteristic of these nanomaterials are their small size, high surface area and massive surface energy. Because of these important characteristic properties, the nanomaterials are different from bulk materials of similar composition regarding physical and chemical properties such as biological, thermal, mechanical, optical absorption, melting point and electrical conductivity. The nanomaterials can be classified into three major categories depending on core source of materials (1) Metal oxide nanomaterials, (2) Metal nanomaterials, (3) Carbon-based nanomaterial.

Metal oxide nanoparticles (MONPs) play a vital role in various fields of physics, chemistry, material science, and medicine [Koch *et al.* (2007)]. Metals can form a variety of oxide compounds. The important distinctive properties of MONPs are their soaring surface energy, enlarged surface area to volume ratio, and strong surface absorption [Santos *et al.* (2016)]. MONPs are zinc oxide nanoparticles, titanium dioxide nanoparticles, iron oxide nanoparticles, cerium oxide nanoparticles, etc. Various methods are utilized for the preparation of metal oxide nanoparticles like thermal decomposition, photolithography, laser ablation, hydrothermal reaction method, chemical vapor methods and biological methods. Different MONPs have different applications. The potential applications of Zinc oxide nanoparticles includes photocatalysis, optoelectronics devices, ceramics industry and laser technology [Lu *et al.* (2015), Yang and Park (2007)]. Titanium oxide nanoparticles are utilized as sensors, cosmetics, printing ink, batteries, water purification, photovoltaics, fuel cells, UV sunscreens, catalysis, optoelectronics, smart windows, and medical implants [El-Naggar *et al.* (2016),

Ramalingam et al. (2019), Ou *et al.* (2016), Chen and Mao (2007), Pakrashi *et al.* (2014), and Abdolmazid *et al.* (2019)]. Iron oxide nanoparticles are used in drug delivery, magnetic resonance imaging (MRI), tissue repair, hyperthermia and have biomedical applications [Gupta and Gupta (2005), Qiao *et al.* (2009), Cano *et al.* (2017), Zhu *et al.* (2018), Tong *et al.* (2017), Laurent *et al.* (2008), Wei *et al.* (2017)]. Cerium oxide nanoparticles exhibited peroxidase-mimetic activity, have catalase oxidase and superoxide oxidase properties as well as used in biomedicine, bioanalysis and drug delivery. [Charbgoon *et al.* (2017), Naganuma (2017)].

Metal nanoparticles (MNPs) are the most widespread nanotechnology-based approach for enveloping biosensors, because of their high surface area, physiological malleability and simplicity. They have unusual shapes having one or more inorganic components. The most commonly used MNPs are palladium nanoparticles (PdNPs), platinum nanoparticles (PtNPs), silver nanoparticles (AgNPs), and gold nanoparticles (AuNPs). The PdNPs are used in electrochemical reactions, hydrogenation, oxidation, carbon-carbon coupling reaction, as a catalyst, gas sensing, as hydrogen storage, and in fuel cell. [Ismail *et al.* (2017), Albani *et al.* (2016), Favier *et al.* (2019), Li *et al.* (2017), Arsiya *et al.* (2017), Kumar *et al.* (2018), Yang *et al.* (2019)]. The PtNPs are utilized in hydrogen storage, fuel cells, catalyst, and as a effective antibacterial agent against both gram-positive and gram-negative bacteria [Bendale *et al.* (2017), Sharma (2017), Tahir *et al.* (2017), Schmidt *et al.* (1999), and Thirumurugan *et al.* (2016)]. AgNPs have unique physical and chemical properties like optical, electrical and thermal, due to this, it is effectively used in medicine, catalysis, wound dressings, keyboard, textile, surgical instruments, water treatment, and biosensing, [Rahban *et al.* (2010), Dubas and Pimpan (2008), Dahl *et al.* (2007), Vivek *et al.* (2012), Filippo *et al.* (2010), Kumar-Krishnan *et al.* (2016), Lu *et al.* (2008), Saxena *et al.* (2012)]. The gold nanoparticles have been utilized in electronic,

biosensing, medicine, catalysis, anticancer, gene delivery, antimicrobial, and antioxidant. [Shen *et al.* (2017), Ribeiro. *et al.* (2017), Varun *et al.* (2017), Farooq *et al.* (2018), Mobed *et al.* (2020), Ramachandran *et al.* (2017), Daniel and Astruc (2004)].

From the last two decades, carbon-based nanoparticles like carbon nano-diamond, carbon nanotube, fullerene, graphene, graphene oxide and fluorescent carbon nanoparticle or Carbon quantum dots have attracted great attention toward the scientific community, because of their dazzling properties and prospective applications. Amid them, carbon quantum dots (CQDs) have attracted growing curiosity in recent years with fascinating properties and have become to a rising star as a novel carbon member. Since in CQDs, all three dimensions lie in the nanometer range. Therefore, it is classified as a zero dimension material. On the other hand, a semiconductor quantum dot uses heavy metals in the fabrication which has certain limitations towards various applications particularly in the biomedical field [Liu *et al.* (2009), Cao *et al.* (2007)]. The heavy metals are extremely toxic even at very low concentrations, which proscribed the study of semiconductor quantum dots in the clinical field [Geys *et al.* (2008)]. The concepts of biocompatible semiconductor quantum dots, synthesized from  $\text{CdClO}_4$  in an aqueous phase, were given by Weller and coworker, which have quite a few limitations like broad size distribution and poor quantum efficiency. Afterward, semiconductor quantum dots were synthesized by Peng *at el* through a greener method from the precursor  $\text{Cd}(\text{acetate})_2$ ,  $\text{CdO}$  and  $\text{Cd}(\text{CO}_3)$ , however have several limits towards biological application. The most significant parameter to overcome these limitations and formulate them for biological applications is the surface modification and functionalization of semiconductor quantum dots. Though, these procedures do not offer always advantage result, and face some major challenges, for instance chemical decomposition, poor photoluminences, high toxicity, photoetching and occasionally

losses their fundamental characteristics. [Lim *et al.*(2015)]. The drawback of semiconductor quantum dots encouraged the conception of carbon quantum dots (CQDs) because of their analogous fluorescence properties, water solubility, low cost, chemical inertness, low toxicity, high and excellent biocompatibility. [Ye *et al.* (2013)].

## 1.2 Carbon Quantum Dots (CQDs)

CQDs were first of all discovered by Xu's Group in 2004, accidentally throughout the purification of single-walled carbon nanotubes [Xu *et al.* (2004)]. CQDs are a category of recently emerged elegant fluorescent nanomaterials which are usually quasi-spherical and core consist of mainly  $sp^2$  and  $sp^3$  hybridized carbon atoms while the external surface includes various functional groups, mainly carboxylic, hydroxyl, carbonyl, amine etc. [Yang *et al.* (2009), Baker *et al.* (2010)]. These functional groups are responsible for chemical stability, outstanding water solubility, excellent quantum yield, surface passivation (doping) and functionalization with various inorganic, organic, polymeric and biomolecules [Sun *et al.* 2006]. The size of CQDs ranges from 1 and 10 nm [Zhou *et al.* (2017), Zuo *et al.* (2016)]. CQDs exhibited a broad peak at around 240 nm, having large surface defect contrast to graphite. This large surface defect arises due to surface passivation (doping) and functionalization of different molecules.

CQDs have attractive features such as good water solubility, ease of synthesis, low cytotoxicity, high photo-stability, high photo-response, good catalysis properties, facile surface functionalization, and tunable excitation-emission. Because of these characteristics properties, CQDs are widely utilized in sensing, catalyst, medical diagnosis, photocatalysis, photovoltaic devices, optronic devices, drug delivery, bio-imaging, laser, single electron transistor, LEDs, and

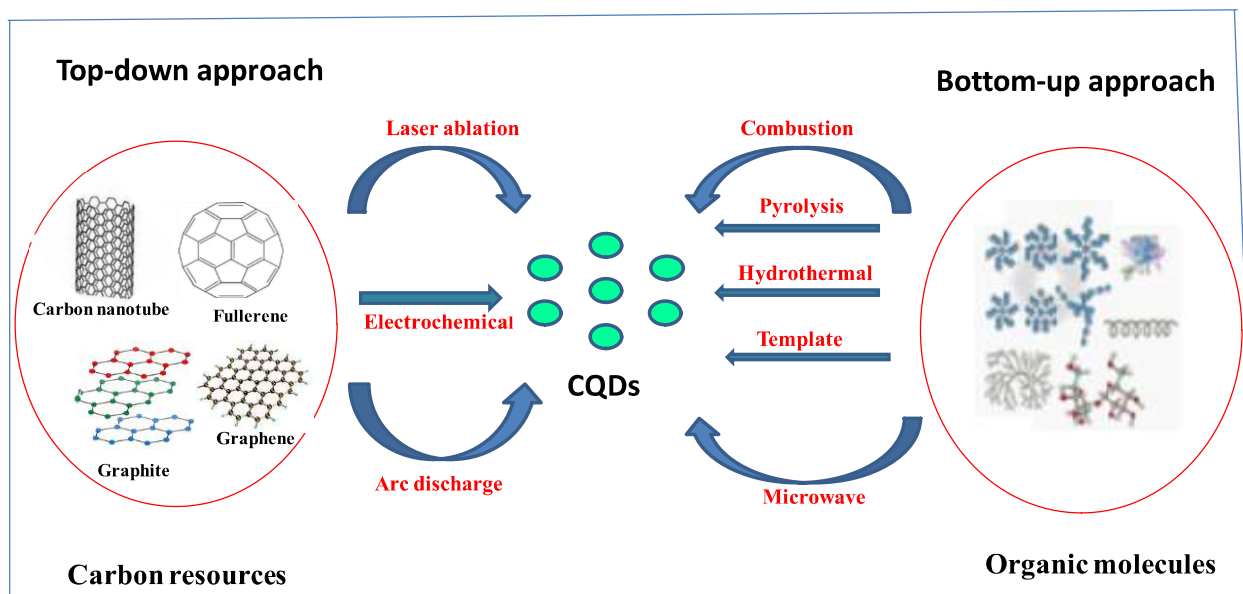
solar cells [Ajayan *et al.* (2001), Baptista *et al.* (2015), Chen *et al.*(2010), Cayuela *et al.* (2016), Pardo *et al.* (2018), Taghavi *et al.* (2020)].

CQDs are synthesized by both, chemical as well as natural precursors. The chemical precursor includes citric acid, ascorbic acid, tartaric acid, sucrose, glucose, glycol, glycerol etc. The natural precursor includes plant leaves, seeds, plant latex, jatropha fruits, orange juice, cocoon silk, pomelo peel, potato, milk, soy milk, banana, soybean, etc. [Zhu *et al.* (2012), Lu *et al.* (2012), Sahu *et al.* (2012), Lu *et al.* (2013), Li *et al.* (2013), Lu *et al.* (2017),] CQDs are also synthesized by surface passivation of organic polymeric moieties like polyethylene glycol, polyethyleneimine, 4,7,10-trioxa-1,13-tridecanediamine, etc [Alam *et al.* (2015)].

### 1.2.1 Methods for the Synthesis of CQDs

CQDs are synthesized by following two approaches- (A) Top-down (B) Bottom-up.

(Scheme 1.1)



Scheme1.1: Diagrammatic illustrations for synthesis of CQDs.

### **1.2.1.1. Top-down approach**

In a top-down approach, the larger carbon resources like carbon nanotubes, fullerene, graphite, grapheme, carbon soot, activated carbon etc. are broken down into more minor constituents with the help of different technique like laser ablation, electrochemical and arch discharge [Yu *et al.* (2005), Sun *etal.* (2006), Zhou *et al.* (2007), Liu *et al.* (2007)]. Though, Top-down approach is extremely helpful and suitable for microsystem industries, it has some limitations like pure nanomaterials can not be obtained from the large carbon precursor and their purification is also costly.

#### **A. Laser ablation**

In the laser ablation technique, the CQDs are synthesized by the irradiation of laser beam on carbonaceous resources. Sun Co-worker in 2006, first of all reported this technique; [Sun *et al.* (2006)]. Q-switched Nd: YAG laser (10 Hz, 1064 nm). The CQDs synthesized by this technique are usually non-fluorescent in nature, heterogeneity in size and have low quantum yield, which influences different potential applications of CQDs. Therefore, to increase the fluorescence properties and quantum yield, pre-treatment like surface passivation (doping) and oxidation are required.

#### **B. Electrochemical method**

Electrochemical method was first described by Zhou and co-worker [Zhou *et al.* (2007)]. In this method, larger carbon precursors are cut down into smaller parts by electrochemical oxidation in the presence of a reference electrode. This method involves a simple synthesis procedures, economical, and high productivity. Zhao *et al.* have prepared fluorescent carbon

nanomaterial by electrochemical oxidation with the help graphite rod as a working electrode [Zhao *et al.* (2008)]. Subsequently, Zheng *et al.* synthesized carbon nanomaterials electrochemically from graphite [Zheng *et al.* (2009)]. Using oxidation method, Deng and Co-worker have synthesized the CQDs from low molecular weight alcohol [Deng *et al.* (2014)]. Electrochemical method has a little benefit like it requires no surface passivation and has a simple purification process.

### **C. Arch Discharge**

Fluorescent carbon quantum dots were first of all discovered by Xu and co-workers accidentally during the separation and purification of single wall carbon nanotube by the Arch discharge method [Xu *et al.* (2004)]. In this process, nitric acid was used as an oxidizing agent to oxidize arch ash, which formed the different functional groups on the surface due to which aqueous solubility increases. The CQDs prepared through this process have smaller sizes and high quantum yield with no surface passivation. Although, CQDs synthesized by this technique have some impurities that are difficult to eliminate because of their complex composition.

#### **1.2.1.2. Bottom up approach**

In bottom-up approach, the smaller carbon resources like atoms and molecules combine to form CQDs by a variety of techniques such as combustion, pyrolysis, hydrothermal/solvothermal, Template and microwave irradiation. This approach strengthens the material chemistry because of their ease operation, less expensive and is easier to implement for the production in large scale [Wang *et al.* (2015)].

#### **A. Combustion method**

In the combustion method, the raw materials used for the preparation of CQDs are

natural gas ash, paraffin putty, and candle ash [Liu et al. (2007)]. Oxidative acid treatment is required in this process which aggregates small carbon resources into CQDs, enhances the aqueous solubility, and controls the fluorescence properties. By using the combustion method, CQDs were first of all synthesized from candle ash by *Liu* and co-workers. The candle ashes were acquired by partial combustion of the candle with aluminum foil and refluxed it in nitric acid solution. When the candle ashes were dissolved in neutral medium followed by centrifugation and dialysis method, the pure CQDs were achieved. The synthesized CQDs by the combustion method have low QY but demonstrate fluorescence without doping.

### **B. Pyrolysis method**

Pyrolysis method is the thermal decomposition of the precursor at elevated temperature in the absence of oxygen. In addition, carbon precursor cleavages into nanoscale colloidal particles in the presence of an alkali and acid concentration. The advantageous properties of this method include practicability, repeatability, and simplicity as well as have high QY. But it is challenging to separate small precursors from raw materials.

### **C. Template method**

CQDs synthesized by the template method, were firstly reported by Bourlinos and co-worker [Bourlinos et al. (2008)]. There are two step in template method (i) Preparation of CQDs in the appropriate template or silicon sphere by calcination.(ii) Etching process occurs to remove the supporting materials. Template method has some advantages like it is simple and apparatus is easily obtainable, surface passivation of

CQDs is suitable, and it also prevents the particles from agglomerating as well as controlling the size of CQDs. The disadvantages of the template method are that it is difficult to separate CQDs from the template, which might influence the purity, particle size, fluorescence property and QY.

#### **D. Microwave synthesis**

Microwave synthesis is a speedy and economical method for the preparation of CQDs via microwave heating. This is simple and convenient compared to other techniques because less time is required to synthesize CQDs with an enhanced quantum yield. Zhu and co-workers have synthesized fluorescent CQDs via heating of poly(ethylene glycol) (PEG-200) and saccharide for 2-10 mins under the microwave (500W) [Zhu *et al.* (2009)]. Microwave synthesis is green, novel, and efficient to synthesize CQDs. Though, there are some limitations like difficulty in separation procedure, purification and non-uniform particle sizes of CQDs restricts their prospective applications.

#### **E. Hydrothermal method**

Hydrothermal method was first of all reported by Zhang and co-workers for synthesizing CQDs from the precursor ascorbic acid [Zhang *et al.* (2010)]. In this method, the precursor molecules are dissolved in an aqueous solvent, kept in Teflon-lined stainless steel autoclave and put in the hydrothermal chamber at high temperature and pressure for a few hours. In this technique, the precursor molecules used are amino acids, proteins, glucose, polymers, polyols, some wastes and natural products [Wang *et al.* (2015)]. During the past few years, hydrothermal method has attracted much attention around the world because of its low cost, single step, ease of operation, non-toxic, and eco-

friendly. CQDs synthesized by hydrothermal methods have various advantageous properties such as water-soluble, monodispersed, highly homogeneous, salt tolerance, controlled particle size, photostable, and show high QY without surface passivation.

Analogous to a hydrothermal method, a solvothermal method is also used for the preparation of CQDs using alcohol, ammonia, and other organic and inorganic solvents instead of an aqueous solvent.

## 1.2.2. Optical properties of carbon quantum dots

### 1.2.2.1 Absorption

CQDs generally shows two absorption bands in the visible region at 280 nm and 350 nm, beside a tail broaden in the UV region. Hu and co-worker reported that CQDs exhibit an absorption peaks at at 280 nm due to a  $\pi-\pi^*$  transition of C=C bond and 350 nm is due to an  $n-\pi^*$  transition of the C=O bond. [Hu *et al.* (2014)]. The location of these absorption band somewhat is different, depending on the raw material and synthesis methodology. Doping of CQDs can also alter the absorption wavelength.

### 1.2.2.2. Fluorescence

The emission of light by a material which has absorbed light is known as fluorescence. The absorbed light is emitted by fluorescent material from the lowest singlet excited state (S1) to singlet ground state (S0). This process is very fast and has nanosecond lifetime. The transitions that occur among two electronic states in fluorescence process are allowed because it has the same spin multiplicity. **(Figure 1.5)**. The fluorescence properties of CQDs have attracted great attention among young researcher because of their several sensing and analytical applications. There is numerous mechanisms have been reported to gain deep insight into the cause of fluorescence in CQDs [Baker *et al.* (2010), Gokus *et al.* (2009); Demchenko *et al.* (2013)].

Among them, following two have been found more prominent. First is that, the fluorescence mechanism is due to band gap transitions arising from the  $\pi$ - conjugated domains ( $sp^2$  hybridized), which is similar to aromatic molecules employing definite energy band gap in favor of absorptions and emissions [Cao *et al.* (2012)]. The second cause of fluorescence origins is related to the surface defect, quantum size effect, carbon core state, surface passivation/functionalization effect and different emissive traps on the surface of CQDs [Fang *et al.* (2011), Shen *et al.* (2011), Li *et al.* (2010), Shen *et al.* (2012)].

The main reason for the surface defect in CQDs are an unsymmetrical allocation of  $sp^2$  and  $sp^3$  hybridized carbon atoms, the existence of heteroatoms like B, N, P, and S. [Gokus *et al.* (2009), Nourbakhsh *et al.* (2010)]. When this surface defect is independently incorporated into the solid host, it creates surroundings similar to aromatic molecules. These molecules can attract UV-light and display various color emissions [Cao *et al.* (2012), Dekaliuk *et al.* (2014)]. CQDs show two types of emission *i.e.* excitation dependent emission (tunable emission) and excitation independent emission. The tunable emission is due to the presence of various emission sites on the surface of CQDs along with particle size distribution, because of this most of the CQDs exhibit tunable emissions [De *et al.* (2013)]. CQDs exhibited extensive and unremitting excitation spectra are highly photostable and have steady fluorescence, contrast to traditional organic dye [Liu *et al.* (2009), Dong *et al.* (2012)].

### 1.2.2.3 Phosphorescence

When the substance emits the absorbed light very slowly, the phenomenon is known as phosphorescence. In phosphorescence, the transition occurs from the lowest triplet excited state (T1) to singlet ground state (S0) *i.e.* forbidden transition occurs according to the spin selection rule. In CQDs, the phosphorescence property is also observed, which was first of all described by

Deng *et al.* via dispersing CQDs to polyvinyl alcohol matrix. The maximum emission obtained was 500 nm with an average life time 380 ns at 325 nm excitation [De *et al.* (2010)]. Phosphorescence in CQDs arises when singlet and triplet state of aromatic carbonyl group in CQDs and polyvinyl alcohol matrix are close in energy to assist spin-orbit coupling which increases the intersystem crossing (ISC).

### **1.2.3. Consequence of doping on the fluorescence intensity of CQDs**

The emission efficiency of CQDs, synthesized by various methods, is relatively low in comparison to conventional semiconductor QDs. Therefore, to improve the emission efficiency of CQDs, the surface passivation (doping) and functionalization are carried out. The doping component could be either metals or non-metal. Mostly, non-metals (heteroatom) are used as doping component because metals cause toxicity in CQDs due to which, it can not be apply in biological field. The heteroatom doping in CQDs might be single or co-doped which enhances the optical property and QY of CQDs.

#### **1.2.3.1. Single heteroatom doping**

##### **(A) Nitrogen (N) doped CQDs**

Doping of N atom in CQDs not only increase the fluorescence efficiency, but also enhance the applications of CQDs in sensing and bioimaging. Both, top-down and bottom-up approaches are used to synthesize nitrogen doped CQDs. Nitrogen-doping may be both natural as well as chemical precursors. Sun and co-worker have synthesized nitrogen-doped CQDs from the grass as a natural precursor through the hydrothermal method [Hsu *et al.* (2012)]. Nitrogen-doped CQDs were also synthesized by (Zhang *et al.*), (Yu *et al.*), (Dong *et al.*) and they reported

that N doped CQDs have more quantum yields than un doped CQDs [Li et al. (2015), Zhu et al. (2012), Wu et al. (2013)].

### **(B). Sulfur (S) doped CQDs**

Doping of sulfur in precursor molecules also increased the fluorescence properties of CQDs. S doping increases the catalytic activity as well as additional applications of CQDs [Dalui *et al.* (2015)]. The S-containing precursors such as thiourea, hydrogen sulfide, sulfuric acid etc, are used in doping of Sulfur [Hu *et al.* (2014), Zhu *et al.* (2009), Liu *et al.* (2012)]. Chandra and co-worker have reported that the S-doped CQDs show fluorescence QY approximately 11.8% high comparable to un-doped CQDs [Chandra et al. (2013)]. Hence, to increase the electronic properties and other large scale applications of CQDs, doping is an admirable and straightforward approach.

### **(C) Phosphorus (P) doped CQDs**

Recently, phosphorus doped CQDs have been effectively synthesized by numerous research groups. Han groups have reported that the doping of phosphorus has change the electronics and fluorescence property of CQDs [Han *et al.* (2015)]. Feng *et al* have prepared P-doped CQDs by using hydroquinone as a C source and phosphorous bromide as P doping [Zhou *et al.* (2014)].

### **(D) Boron (B) doped CQDs**

The catalytic activities as well as the electronic properties of CQDs have been increased by doping of Boron element. Feng and co-worker have synthesized B-doped CQDs from

hydroquinone as C source and  $\text{BBr}_3$  as B source. The QY obtained was 14.8% and displayed intense blue fluorescence having charge transfer in CQDs [Shan et al. (2014)]. In addition, using hydrothermal and microwave methods, Lu *et al.* and Bourlinos *et al.* have synthesized B-doped CQDs with QY 22 % and 10-15%, respectively [Xu *et al.* (2016)].

### 1.2.3.2 Multiple heteroatom doping

#### (A) N and P co-doped CQDs

First of all, Sahu *et al.* have reported N and P co-doped CQDs having QY of about 59% [Li *et al.* (2015)]. Further, Zhang *et al.* and Sun *et al.* synthesized fluorescent N, P doped CQDs, which have higher QY than un-doped CQDs [Gong et al. (2016), Sun et al. (2015)]. Because of the combine effect, heteroatom-doped CQDs display significant QY compared to un-doped CQDs.

#### (B) N and S co-doped CQDs

Dong and co-worker have first of all prepared N and S co-doped CQDs from citric acid and L-cytokine by hydrothermal method. The QY obtained was very high (73%) [Dong *et al.* (2013)]. N and S co-doped CQDs were further reported by Zhao and colleagues by using ammonium thiocyanate as carbon, sulfur and nitrogen source with high QY 74.15%. These results revealed that N, S doped CQDs not only improve the QYs but also broaden their applications like nanomedicine, catalytic activity, bioimaging, and biosensing [Xue *et al.* (2016)].

#### (C) N and B co-doped CQDs

Doping of B and N atom in chemical as well as in natural sources have significantly influenced the optical properties of CQDs and enhanced their extensive variety of applications [Jana *et al.* (2013)]. Kanwal and co-worker synthesized fluorescent CQDs through hydrothermal method by doping N-(4-hydroxyphenyl) glycine as N source and boric acid as B source with QY about 11.44% [Jahan *et al.* (2013)].

### **1.3. Fluorescence quenching**

When the emission intensity of fluorescent molecules decreases, then this phenomenon is known as quenching. Quenching occurs when fluorescent molecules interact with quencher molecules i.e. analyte. Most commonly used quencher molecules are iodide ions, metal ions, molecular oxygen, amino acids and acrylamide [Phillips *et al.* (1986)]. The quenching procedure occurs depending upon the interaction of fluorescent molecules (CQDs) to quencher molecules that includes inner filter effect (IFE), static quenching, and dynamic quenching.

#### **1.3.1. Inner filter effect**

When a fine and precise spectral overlapping occurs between the absorption spectrum of fluorescent molecules and quencher molecules, then the quencher molecules absorb the emission light of fluorescent molecules, which results in the quenching of fluorescent molecules. This process is called the inner filter effect (IFE) [Yuan *et al.* (1987)]. IFE mechanism is generally shown by toxic metal ions because they have wide absorption spectrum.

#### **1.3.2. Static quenching**

In static quenching, the emission intensity decreases when ground state interaction occurs between fluorescent molecules and quencher molecules [Feng *et al.* (2016)]. Ground state

interaction is confirmed by fluorescent life time measurement experiment. In this experiment, the life time of fluorescent molecules (CQDs) is recorded in the presence and absence of quencher molecules. If there will be no obvious shift in average life time then ground state interaction occurs between the CQDs and quencher molecules. This reveals the static quenching. The determination of binding attraction between the CQDs and quencher molecules is denoted by following standard Stern-Volmer plot **equation (1.1)** .

$$F_0/F = 1 + K_{sv}[Q] \quad (1.1)$$

Where  $F_0$  is the fluorescence intensity of CQDs and  $F$  is the fluorescence intensity of CQDs in the presence of quencher molecules.  $[Q]$  is the concentration of quencher molecules and  $K_{sv}$  is Stern-Volmer quenching constant. In static quenching mechanism, as the temperature increases, the quenching constant  $K_{sv}$  decrease.

### 1.3.3. Dynamic quenching

In dynamic quenching, the emission intensity decreases when excited state interaction occurs between fluorescent molecules and quencher molecules. During life time measurement experiments, if there will be obvious shift in the average life time, then excited state interaction occurs between the CQDs and quencher molecules, resulting in the dynamic quenching. This is also known as collisional quenching. Because of increase in the diffusion rate, the value of Stern-Volmer constant ( $K_{sv}$ ) increases on increasing the temperature.

### 1.4. Fluorescence quantum yield (QY)

The ratio of number of emitted photon divided by the number of an absorbed photon is known as QY (**Equation (1.1)**). The classic value of QY will be less than one because all absorbed photons

do not direct to product formation. Though, in case of photo-induced or radiation-induced chain reactions, the value of QY may be greater than one.

$$\text{Quantum yield (QY)} = \frac{\text{Photon emitted}}{\text{Photon absorbed}} \quad \mathbf{1.1}$$

The QY of fluorescent materials (CQDs) is determined with respect to quinine sulfate as a standard reference.

### **1.5. Applications of CQDs**

CQDs possess good water solubility, small size, high resistance to chemical, high photo stability, low cytotoxicity, high surface to volume ratio and distinctive optical properties. Because of these unique properties, CQDs have been applied in various fields such as sensing of heavy metal ions, sensing of amino acids, Schottky Barrier Diodes (SBD), peroxidase mimetic enzyme activity, light emitting devices, chemical sensor, biosensor, photo catalysis, temperature sensor, drugs delivery, cell imaging, fluorescent ink, Sensing of pesticides and fungicides and so on.

#### **1.5.1. Peroxidase-mimetic enzyme activity**

Horseradish peroxidase (HRP) is a natural enzyme. Similar to HRP, carbon-based nanoparticles like graphene, graphene oxide, Au nanocluster (NC)–graphene oxide, Au–carbon nitride and single wall carbon nanotubes shown peroxidase mimetic enzyme activity. [Hao *et al.* (2013), Lin

*et al.* (2015)]. The other carbon-based nanoparticles, like metal oxide nanoparticles, carbonnitride, and Fe/N-doped carbon were also used as a peroxidase-mimetic enzyme activity [Sun *et al.* (2010), Wang *et al.*(2013), Tian *et al.* (2013), Liu *et al.* (2017), Pavlovic *et al.* (2018)]. Heteroatom doped fluorescent CQDs also exhibit peroxidase-mimetic enzyme activity [Deng *et al.* (2016), Gong *et al.* (2009), Jiang *et al.* (2017)]. But there are some limitations of these carbon-based nanomaterials such as multistep synthesis and used of caustic materials. Therefore, we have synthesized fluorescent carbon quantum dots from natural source i.e. *Azadiracta indica* leaves through one-pot hydrothermal method which showed peroxidase-mimetic enzyme activity. As prepared N-CQDs exhibited excitation-dependent emission spectra with high QY of 27.2%. For the oxidation of TMB, The catalytic activities of N-CQDs were based on H<sub>2</sub>O<sub>2</sub> concentration, therefore it was used for colorimetric detection of H<sub>2</sub>O<sub>2</sub> with LOD 0.035 mmol/L. The ox-TMB acted as a probe for the detection of Ascorbic acid (AA) and the LOD was calculated to be 1.773 μM. Addition to this, sensing of AA was also performed in biological samples [Yadav *et al.* (2018)].

### **1.5.2. Sensing of tyrosine**

Tyrosine (4-hydroxyphenylalanine) is a non-essential amino acid. It is a significant ingredient of proteins and plays a vital task in most of biochemical reactions [Habibi *et al.* (2016)]. During a stressful situation, tyrosine helps to improve learning memory, alertness and may even regulate mood. The deficiency of tyrosine results in albinism, hypochondria and depression, while excess concentration causes Parkinson's disease or dementia [Castrén *et al.* (2005), Shadjou *et al.* (2018)]. Hence, it is important to detect tyrosine concentration effectively and efficiently. Some metal nanoparticles such as AuNPs, CuO–NPs, CeO<sub>2</sub> nanoparticles, etc. were used for the

detection of tyrosine. [Yola *et al.* (2015), Razmi *et al.* (2011), Razavian *et al.* (2014)]. Carbon-based nanoparticles like graphene quantum dots were also used for the detection of tyrosine [Li *et al.* (2016)]. Recently we have synthesized fluorescent CQDs through one-pot hydrothermal treatment by using polyethyleneimine as N source and latex of *Ficus benghalensis* as C source. The synthesized CQDs exhibited green colour, so named as G-CQDs. It shows excitation-dependent emission spectra. The QY was calculated to be 41.2%. G-CQDs sensed tyrosine selectively and sensitively. The LOD was calculated to be 0.13  $\mu\text{M}$ . Addition to this, we have also detect tyrosine in milk samples [Yadav *et al.*(2021)].

### 1.5.3. Cell imaging

The important characteristic of CQDs is that they are environment-friendly and non-toxic. Therefore, can be used *invitro and invivo* both [Mehta *et al.*(2014)]. Generally, CQDs are non-toxic but after surface passivation, they may cause cytotoxicity. Hence it is necessary that, for cell imaging applications, the surface passivating agent should not be toxic [Wang *et al.* (2011)]. First of all, cell viability experiment is carried out via treating the cell line with various CQD concentrations. The biocompatibility and cytotoxicity results confirmed the application of CQDs in cell imaging. Sun and co-worker have described the cell imaging applications of CQDs *in vitro* and *in vivo* [Sun *et al.* (2006)]. By using multimodal imaging technology, Yang and co-worker have reported the application of CQDs as a fluorescence contrast agent in mice, which included optical imaging modalities and Magnetic Resonance Imaging (MRI) [Yang *et al.* (2009)]. Optical imagings recommend rapid screening whereas MRI communicates the anatomical and physiological information with high resolution. Further, multimodal bioimaging application of iron oxide doped CQDs (IO-CQDs) were studied by Srivastava and co-worker [Srivastava *et al.* (2012)]. Additions to this, the application of CQDs in a cell imaging were also

reported by numerous research group [Cao *et al.* (2007), Hsu *et al.* (2013), Singh *et al.* (2019)]. We have also reported the application of CQDs in cellular imaging. First of all, MTT assay was carried out on SH-SY5Y neuroblastoma cells. The cell viability was found up to 80 %. These results exposed that GB-CDs have negligible cytotoxicity and can be used in intracellular imaging [Yadav *et al.* (2019)].

#### **1.5.4. Sensing of fungicides and pesticides**

The substances which kill the fungus are known as fungicides and the substances which kill the pests are known as pesticides. The low concentration of fungicides and pesticides may affect the human health. Therefore, it is requires the sensing of fungicides and pesticides effectively and sensitively. In the latest years, fungicides and pesticides have been detected by CQDs effectively. Li and co-worker have synthesized N and S co-doped CQDs using pyrolysis method for the detection of carbaryl (pesticide) with LOD  $5.4 \times 10^{-9}$  g/L [Li *et al.* (2016)]. In addition, Li *et al.* have synthesized N and P co-doped CQDs to detect carbendazim (a fungicide). The LOD was found to be 0.002  $\mu$ M [Yang *et al.* (2018)].

#### **1.5.5. Drug delivery**

Recently, the application of nanomaterials in the drug delivery system has attracted much attention. The uses of gold nanoparticles in drug delivery systems are widely explored. Though, the toxic nature of gold nanoparticles restricts their applications in clinical therapy [Alkilany *et al.* (2010)]. In addition, there is strong affinity occurs between the gold nanoparticle and thiol group, which also limits their application towards the drug delivery systems [Kumar *et al.* (2013)]. Hence, because of the rapid, simple and economical synthetic method, CQDs are excellent substitutes over gold nanoparticles. The good surface passivation properties and high

surface area of CQDs offer an admirable platform for drug conjugation and expand the choice for drug delivery systems. CQDs are also utilized as drug vehicles in biological systems due to their nontoxicity and biocompatibility. The fluorescence signal of CQDs monitored the distribution of anticancer drugs *in vivo* by conjugating the drugs on its surface. By adhering the oxidized oxaliplatin on the surface of CDs (CD-Oxa), Zheng and co-worker have synthesized the multifunctional theranostic agent. They showed that CD-Oxa possesses anticancer property and superior bioimaging. [Zheng *et al.* (2014)]. Kim *et al.* have doped CQDs into gold nanoparticles to deliver the DNA into the cells and on the surface of CQDs-gold nanoparticle, conjugated the PEI-pDNA. [Kim *et al.* (2013)]. Panday and co-worker have prepared CQDs functionalized gold nanorods and applied in photothermal therapy, for the delivery of doxorubicin, and in bioimaging [Pandey *et al.* (2013)]. In addition, Thakur *et al.* have prepared a broad spectrum antibiotic, ciprofloxacin affixed to CQDs. These offered an efficient nanocarrier under physiological conditions for the controlled release of drugs [Thakur *et al.* (2014)].

#### 1.5.6. Schottky barrier diodes (SBD)

Schottky barrier diode, also known as schottky diode, hot-carrier diode or low voltage diode is a type of metal-semiconductor junction diode. The important characteristics of schottky barrier diode are that it has fast switching action and low forward voltage drop. When p-type and n-type semiconductors are joined together then PN junction diode is formed while in schottky diode, p type semiconductors are replaced by metals such as silver, platinum or aluminium. Kaufmann *et al.* have synthesized Zinc oxide nanoparticles (ZnO NP) and determined Schottky Barrier Height (SBH) and give an idea about thin film transistors [Kaufmann *et al.* (2021)]. Sanghania and *co-worker* have prepared iron oxide ( $\text{Fe}_2\text{O}_3$ ) nanoparticles and utilized them as

schottky barrier diodes [Singhania *et al* (2020)]. Abbas *et al.* have synthesized gold nanoparticles for the fabrication of schottky barrier diodes [Abbas *et al.* (2020)]. However, fabrication of schottky barrier diode from CQDs was not reported. We have recently prepared green fluorescent CQDs (G-CQDs) and fabricated a schottky barrier diode by using the optical properties of G-CQDs. First of all, metal (Ag)-semiconductor (G-CQDs) junction diode was fabricated on indium doped tin oxide (ITO) coated glass substrates. After then G-CQDs was deposited on the ITO coated glass. When the desired thickness of G-CQDs (B100 nm) was obtained, B80 nm thick metal (Ag) was deposited for a contact electrode. We also investigated the current-voltage (I–V) characteristics of the device. The semiconductor parameter analyser from -1.5 V to +1.5 V was used for the (I–V) measurements of G-CQD based thin-film device. Depending upon the I–V characteristics of Ag/G-CQD thin-film device, a nonlinear rectifying behaviour was exhibited by the interface between Ag/G-CQDs, which confirm the fabrication of a Schottky Barrier Diode [Yadav *et al.* (2021)].

### **1.5.7. Light emitting devices**

The light emitting behaviour of CQDs is strong and stable. Because of this, it is used in the fabrication of light emitting devices (LED's) [Guo *et al.* (2012)]. Nitrogen rich CQDs have broad and bright visible light emission properties under UV- illumination, therefore widely utilized for phosphor application [Kwon *et al.* (2013)]. A film of CQDs is embedded on the polymer for the fabrication of LED's and the mechanical support is provided by polymer matrix which also prevents the solid state quenching of CQDs. The films obtained are ecofriendly, highly flexible, mechanically robust, cost-effective, thermally stable, and effectively used in LED's [Mao *et al.*(2014)]. Recently, doped and un-doped CQDs have been utilized in LED's. Khan and co-

worker have synthesized N-doped CQDs and polyvinyl alcohol (PVA) composite for the development of green LED. The precursors used for the preparation of CQDs were urea and ammonium citrate and afterward emerged into a PVA matrix [Khan *et al.* (2018)]. White LED was designed by Zhou *et al.* with the help of N and S co-doped CQDs and epoxy resin [Zhou *et al.* (2017)].

#### **1.5.8. Solar cells**

The devices which convert the energy of light (solar energy) directly into electricity by photovoltaic effect are called solar cells. Solar cells are semiconductor devices that use sun light to produce electricity. The photons emitted by sun's rays are absorbed by silicon present in solar cells. The promising generation of solar cells includes dye-sensitized solar cells, polymer-based solar cells, perovskite-based solar cells and nanocrystal-based solar cells. CQDs have been revealed to be ideal candidates for the photovoltaics in solar cells [Ciambelli *et al.* (2018)]. Zhang *et al.* have synthesized N-doped CQDs as metal-free sensitizers in dye-sensitized solar cells (DSSCs). The CQDs-sensitized titanium oxide (TiO<sub>2</sub>) electrode was organized by the hydrothermal method for 4 h at 100 °C between TiO<sub>2</sub> and N-doped CQDs [Zhang *et al.* (2013)]. Wang and co-worker have also fabricated solar cells (DSSC) through sandwiching gel electrolytes between a platinum (Pt) counter electrode and TiO<sub>2</sub> electrode sensitized N-doped CQDs [Wang *et al.* (2016)].

#### **1.5.9. Sensing of heavy metal ions**

If the specific gravity of metallic elements will be more than  $5 \text{ g/cm}^3$ , then the metals are called heavy metal ions. These metal ions include metalloids, transition elements, lanthanides and actinides [Jares *et al.* (2003)]. Arsenic (As), Lead (Pb), Chromium (Cr), Iron (Fe), Copper (Cu), Nickel (Ni), Zinc (Zn), Cadmium (Cd), Mercury (Hg) [Lambert *et al.* (2000)]. Amid these heavy metals Cr, Hg, Pb, As, and Cd, have very bad effect on human health still in very small concentration and result in mutagenic disorders [Flora *et al.* (2008), Gajalakshmi *et al.* (2012)]. Though, some heavy metal ions like Fe, Ni, Cu and Zn are crucial for the physiological function of the human body. The toxicity of heavy metal ions is a major warning to human beings as well as the environment. The major challenge for the growing population is the continuous increase in exposure of heavy metals ions. The natural resources as well as human activities, are responsible for the contamination of heavy metal ions in soil and water bodies. Natural resources include earthquake, soil erosion, natural weathering of the earth crust, volcanic eruption etc. Human activities includes industrial effluents, insect controlling chemical agent mining, sewage discharge, urban runoff, etc. [Morais *et al.* (2012)].

The heavy metal ions contaminate the drinking water and affect the human being as well as flora and fauna. The whole ecosystem is adversely affected by the incorporation of heavy metal ions into the microbial world and plants.

#### **1.5.9.1. Sensing of Fe (III)**

In biological systems, iron (Fe) is considered the most significant transition metal and is the fourth richest element in the earth crust. It is a crucial component of hemoglobin which assists the transport of blood in the human body. The scarcity of iron results in many health problems

in a human beings like frequent fatigue, loss of appetite, anemia, decreased immunity and reduced work routine while the excess concentration of iron in the blood causes various biological disorders like tissue damage of unusual organs, deterioration of lipids, proteins, and nucleic acids. Hence, it is necessary to determine the concentrations of iron in biological fluids. Ferric ion ( $\text{Fe}^{3+}$ ) is roughly a ubiquitous metal ion in biological and environmental systems. For the detection of  $\text{Fe}^{3+}$ , Zhu *et al.* synthesized CQDs-based nanoprobe with a limit of detection (LOD) 0.55 ppm [Yang *et al.* (2014)]. Addition to this, N-doped CQDs were prepared by Chen and co-worker for the detection of  $\text{Fe}^{3+}$  with LOD 2.5 nM. Subsequently, highly fluorescent N and P co-doped CQDs were synthesized by Chandra *et al.* to detect  $\text{Fe}^{3+}$  in cancer cells [Chandra *et al.* (2016)]. N-doped CQDs were further synthesized by Li *et al.* for the sensing of  $\text{Fe}^{3+}$  with LOD 0.001 M [Xu *et al.* (2017)]. We have also synthesized fluorescent GB-CDs from *Artocarpus lakoocha* seeds by using one pot hydrothermal method for the detection of  $\text{Fe}^{3+}$ . The LOD was calculated to be 0.62  $\mu\text{M}$ . Further we have detected the  $\text{Fe}^{3+}$  in real samples such as human blood serum and river water [Yadav *et al.* (2019)].

#### **1.5.9.2. Sensing of Hg (II)**

Hg is renowned as a hazardous metal and is one of the most toxic pollutants. Hg badly influences the whole ecosystem, particularly a human body and other flora and fauna. The major route of Hg poisoning in human beings is the utilization of Hg contaminated food specially fish. In Japan (1956), mercury-contaminated fish caused world famous Minamata disease. Even low concentrations of Hg causes liver damage expiratory dyspnoea, headaches, gastrointestinal problem, neurological disorder, microtubule destruction, hyperspasmia, muscle destruction,

kidney failure, renal failure, and so on [Technouwou *et al.* (2003), Nolan *et al.* (2008) Gajalakshmi *et al.* (2012), Gong *et al.* (2014)]. Therefore, selective and sensitive detection of Hg is necessary. Yuan and co-worker have synthesized blue emitting CQDs from TTDDA and citric acid in glycerol by pyrolysis method for the detection of Hg<sup>2+</sup> [Yuan *et al.* (2014)]. The LOD was 4 ppb. In other experiments, Zhang *et al.* have prepared blue-fluorescence N-doped CQDs from folic acid as carbon and nitrogen precursors by using the hydrothermal method for the detection of Hg<sup>2+</sup>. The LOD was calculated to be 0.23 μM and QY obtained was 15.7% [Zhang *et al.* (2014)]. Our research groups have also prepared N-doped fluorescent CQDs for the selective and sensitive detection of Hg<sup>2+</sup> by one-pot hydrothermal method. The LOD was found to be 0.085 μM. The as synthesized N-CQDs exhibited excitation-dependent emission spectra with fluorescent QY 41% [Singh *et al.* (2019)]. Further, N-CQDs + Hg<sup>2+</sup> turn-off solution was used for the turn-on sensing of glutathione. This on-off-on sensing system was used for the implication of the logic gate. Additions to this, N-CQDs were also utilized in cell imaging.

### 1.5.9.3. Sensing of Cr (VI)

Chromium (VI) is extremely toxic and carcinogenic to a human being even in very small concentrations. Presently, CQDs have been widely used for the sensing of Cr (VI). Zheng and co-worker have prepared N-doped CQDs for the sensing of Cr (VI) which involves inner filter effect (IFE) mechanism for fluorescence quenching [Zheng *et al.* (2013)]. Omer groups have also prepared N and P co-doped CQDs that selectivity detects Cr (II) ions through a quenching mechanism. The LOD was calculated to be 0.1 μM [Omer *et al.* (2019)]. Our research groups have also prepared N and P co-doped CQDs via one-step hydrothermal method for the

detection of Cr (VI) selectively and sensitively. The as-prepared N,P-CQDs exhibited excellent fluorescence properties with a high QY of 73% [Singh *et al.* (2018)].

#### 1.5.9.4. Sensing of Co (II)

Co is the active centre of a group of co-enzymes called cobalamins (Vitamin B<sub>12</sub>). It plays an important role in the implementation red blood cells (RBC's) as well as the maintenance of nerve cells. Hence the selective and sensitive detection of Co is imperative. Chang *et al.* have synthesized fluorescent CQDs for the detection of Co<sup>2+</sup>. The LOD was found to be 5 nM [Cheng *et al.* (2015)]. Additions to this, our research groups have also prepared N-doped CQDs from glycine and polyethyleneimine by using the hydrothermal method to detect Co<sup>2+</sup> ion. The LOD was calculated to be 0.12 mM [Bano *et al.* (2019)].

#### 1.5.10. Photocatalysis

Recently in organic synthesis, photocatalytic processes have attracted great attention as a greener alternative because sunlight is an effective limitless energy [Kumar *et al.* (2008)]. CQDs have a smaller size and high surface area, therefore used as photocatalysts in organic synthesis. Further Ma *et al.* have reported that photocatalytic properties can be tuned by the surface passivation of CQDs. [Ma *et al.* (2012), Hu *et al.* (2013)]. Lately, Liu and co-worker have described the photochemical property of AuNP-CQDs composites which are responsible for the photochemical oxidation of cyclohexane into cyclohexanone under visible light at room temperatures in the presence of H<sub>2</sub>O<sub>2</sub> [Die *et al.* (2015)]. An effective photocatalyst TiO<sub>2</sub> is used to split water and produce hydrogen energy. Li *at el.* have synthesized nanocomposite TiO<sub>2</sub>-

CQDs to degrade methylene blue under visible light [Li *et al.* (2010)]. The superior photocatalytic behaviour of TiO<sub>2</sub>-CQDs is because of the presence of long live holes on the surface which enhances their photo catalytic behaviour [Lim *et al.* (2015)]. In addition, other nanocomposite like Fe<sub>2</sub>O<sub>3</sub>-CQDs, Cu<sub>2</sub>O-CQDs, Ag<sub>3</sub>PO<sub>4</sub>-CQDs, and ZnO-CQDs, were also described by various research groups which show photocatalytic activity [Li *et al.* (2012), Zhang *et al.* (2012), Yu *et al.* (2012)].

### 1.5.11. Biosensor

Due to easy surface passivation, high photostability, excellent biocompatibility, high water solubility, non toxicity, excitation dependent emission properties, and good cell permeability, CQDs are used for the detection of Potassium, iron, copper, glucose, glutathione, cellular, pH, and nucleic acid [Zhao *et al.* (2011), Li *et al.* (2011), Shi *et al.* (2011), Wei *et al.* (2012)]. Depending upon the quenching and recovery of the fluorescence of CQDs, the nucleic acid was detected by single-stranded DNA (ss-DNA) which was adsorbed on CQDs surface by  $\pi$ - $\pi$  interaction resulting in the quenching of the fluorescence. Further, fluorescence recovery signal was observed when ss-DNA hybridized to double stranded DNA (ds-DNA) which was removed from CQDs surface [Zhao *et al.* (2011)]. In addition, CQDs was utilized to detect bacterial cell in sewage water and miniature bio-analyte such as, ascorbic acid, glucose, mitochondrial H<sub>2</sub>O<sub>2</sub> antibacterial drugs, dopamine, glutathione etc [Mao *et al.* (2012), Zheng *et al.* (2013), Huang *et al.* (2013), Niu *et al.* (2014)]. Our research groups have also detected glutathione from N-CQDs. The N-CQDs were synthesized by hydrothermal method. The fluorescent QY obtained was 41% with respect to quinine sulfate as standard. Due to excellent optical properties of N-CQDs, it was used for the turn-off detection of heavy toxic metal Hg<sup>2+</sup> ion. The LOD was calculated to be 0.08  $\mu$ M. Further, when we added different concentrations of glutathione in the quenched

solution of N-CQDs+Hg<sup>2+</sup>, the fluorescence was recovered, revealing the selective sensing of glutathione. The LOD was found to be 2.0 μM. [Singh *et al.* (2019)].

#### **1.5.12. Temperature sensor**

The application of CQDs as a temperature sensor has been extensively used in recent. Han and co-worker have synthesized blue fluorescent N and S doped co-doped CQDs from the precursor's sodium citrate and thiourea. The QY obtained was 26.9%. The synthesized CQDs were used for temperature detection. As the temperature increases from (5-70 °C), the fluorescence emission intensity decreases gradually [Han *et al.* (2019)]. The fluorescence quenching of CQDs were probably because aggregation of CQDs with rise in temperature. Shi *et al.* have prepared N and S co-doped CQDs and utilized as an efficient temperature sensor. [Shi *et al.* (2017)]. Recently, Zuo and co-worker have used N and S co-doped CQDs as an effective temperature sensor because the synthesized CQDs exhibited temperature dependence fluorescence emission spectra [Zuo *et al.* (2019)].

#### **1.5.13. Fluorescent ink**

The excellent properties of CQDs make its use in fluorescent ink. Guo and co-worker synthesized B and N co-doped CQDs, and used them as fluorescent ink in writing letters/numbers/characters [Guo *et al.* (2017)]. The color of letters changes from light yellow to colorless in visible light by decreasing the different concentrations of CQDs. Furthermore, these CQDs displayed blue color under UV-light at excitation wavelengths of 365 nm and showed fluorescence stability up to three month, revealing their potential application in fluorescent ink for anti-counterfeiting. Similarly, Bandi *et al.* have synthesized fluorescent N and S doped CQDs and utilized them as anti-counterfeiting in fluorescent ink [Bandi *et al.* (2018)].

## 1.6. Motivation of the study

CQDs are a rising star and the new class of zero-dimensional carbon nanomaterial with sizes ranging from 1 to 10 nm. CQDs have excellent optical properties. There are two methods utilized for the synthesis of CQDs. First one is the Top-down and second is the Bottom-up approach. Top-down method has some limitations like utilization of bulky precursors, complex synthetic procedures and also purification cost is high. On the other hand, in Bottom-up method small organic precursors are used. In bottom-up approach, several methods are utilized but most of them possess some limitations like the requirement of post-surface passivation, multistep synthesis, time-consuming process and low fluorescent quantum yield. On the other hand, the hydrothermal method is superior because it is a one-step process, less time-consuming, ecofriendly, no requirement of post passivation and is non-toxic. Further, we have used the synthesized CQDs as peroxidase mimetic activities, sensing of  $H_2O_2$  and ascorbic acid, sensing of iron (III), cell imaging, sensing of tyrosine and fabrication of schottky barrier diode.

## 1.7 Research Objectives

From the above-mentioned background information and extensive literature survey, the aim of this research work is to synthesize fluorescent CQDs by the use of the fluorimetric and colorimetric methods and utilize it for sensing applications. Therefore, the major objectives of this thesis work are as follow:

- ❖ To synthesize fluorescent CQDs with high QY from the different natural precursors such as *Azadirachta indica* leaves, *Artocarpus lakoocha* seeds, the latex of *Ficus benghalensis* by using one-step hydrothermal method.
- ❖ Characterization of these fluorescent materials through different instrumental techniques such as-
  - ❖ Transmission Electron Microscopy (TEM)
  - ❖ X-Ray Diffraction Spectroscopy (XRD)
  - ❖ Fourier Transform Infrared Spectroscopy (FTIR)
  - ❖ X-Ray Photoelectron Spectroscopy (XPS)
  - ❖ UV-Visible Spectroscopy
  - ❖ Fluorescence spectroscopy
  - ❖ Time-resolved fluorescence life time spectroscopy
- ❖ To utilize fluorescent CQDs as peroxidase-mimetic enzyme activity and colorimetric detection of H<sub>2</sub>O<sub>2</sub> and Ascorbic acid.
- ❖ To utilize fluorescent CQDs for the sensing of Fe (III) in an aqueous medium as well as in living cells.
- ❖ The potential feasibility was explored in a real natural sample.
- ❖ Utilization of fluorescent CQDs for the sensing of Tyrosine (Tyr) and fabrication of Schottky Barrier Diodes.