“SYNTHESIS OF DUAL EMISSIVE CARBON QUANTUM DOTS FOR SENSING APPLICATIONS”

A Thesis submitted

In

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in

Chemistry

Submitted by

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PATIALA, 147004

2018

CERTIFICATE

This is to certify that the thesis entitled **"Synthesis of Dual Emissive Carbon Quantum Dots for Sensing Applications"** submitted by **Ms. Aditi Dewan** in the partial fulfillment of the requirements for the degree of Master of Science in Chemistry from Thapar Institute of Engineering & Technology, Patiala is a bonafied piece of work carried out under the supervision of **Dr. Soumen Basu** Associate Professor, School of Chemistry & Biochemistry, Thapar Institute of Enginering &Technology, Patiala and no part of the matter embodied in this report has been submitted to any other university or institute for the award of any degree.

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It is certified that the above statement made by the student is correct to the best of my/our knowledge and belief.

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DECELARATION

I hereby declare that the thesis entitled **"Synthesis of Dual Emissive Carbon Quantum Dots for Sensing Applications"** is an authentic record of my work carried out as requirements for the award of the degree of Master of Science in Chemistry at Thapar Institute of Engineering and Technology, Patiala under the supervision of **Dr. Soumen Basu,** Associate Professor, School of Chemistry & Biochemistry, Thapar Institute of Engineering and Technology, Patiala during July' 2016 to July' 2018. No part of the matter embodied in this report has been submitted to any other university or institute for the award of any degree.

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ABSTRACT

Carbon quantum dots (CQDs), a new class of nano-material with unique optical property and have great potential in various applications. This work demonstrated the possibility of tuning the emission wavelength of CQDs by simply changing the acid type used during synthesis. In particular, a mixture of sulfuric and phosphoric acids were used to carbonize the same starting precursor, sucrose. This resulted in the isolation of CQDs with green (434 nm) and yellow (520 nm) emission when excited at 350 nm. Solvatochromic effects was studied systematically using photoluminescence spectra (PL) and the origin of PL shifts of the CQDs in different solvents was discussed in regard to the contribution from hydrogen bonding and dipole–dipole interactions. A turn-on/off strategy was proposed for specific recognition of melamine. Initially on the basis of energy transfer process, selectivity of the CQDs was investigated towards different cations. CQDs were found selective only for Fe^{3+} ions. The sensitivity of CQDs-Fe^{3+} ions system was also evaluated for melamine detection and found that CQDs-Fe^{3+} ions mixture was selective for melamine.

Key Words:

Carbon quantum dots, Photoluminescence, Solvatochromatic effect, Turn-on/-off fluorescence, Limit of Detection.

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LIST OF ABBREVIATIONS AND SYMBOLS

1. NPs	Nanoparticles
2. λ_{max}	Maximum wavelength
3. λ_{ex}	Excitation Wavelength
4. QSE	Quantum size effect
5. nm	Nanometer
6. QDs	Quantum dots
7. EBR	Excition bohr radius
8. >	Greater than
9. <	Less than
10. CQDs	Carbon Quantum dots
11. SWCNTs	Single-walled carbon nano-tubes
12. PL	Photoluminescence
13. CND	Carbon Nanodots
14. GCQD	Graphene carbon quantum dots
15. PD	Polymer dots
16. ^{o}C	Degree Celsius
17. µL	micro liter
18. µM	micro molar
19. M	molar
20. mL	milli liter
21. FRET	Fluorescence resonance energy transfer
22. AuNPs	Gold Nanoparticles
23. QY	Quantum yield
24. HR-TEM	High resolution transmission electron microscope
25. LOD	Limit of Detection
26. H_2O	Water
27. MeOH	Methanol
28. DMF	N,N-dimethyl formamide
29. ACN	Acetonitrile

30. HSAB	Hard-soft-acid-base
31. LM	Lipert Mataga
32. KT	Kamlet Traft
33. HBA	Hydrogen bond accepting ability
34. HDA	Hydrogen bond donating ability
35. g	grams
36. UV	Ultra Violet
37. Oxa	Oxaliplatin
38. EDC	1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide
39. NHS	N-Hydroxysuccinimide
40. PEG	Polyethylene glycol
41. CNPs	Carbon nanoparticles
42. PPEI-EI	Propionylethylenimine-co-ethylenimine
43. CTAB	Cetyl trimethyl ammonium
44. MOFs	metal organic frameworks
45. AE-TPEA	N-(2-aminoethyl)-N,N,N´-tris-(pyridine-2-ylmethyl)ethane-1,2-diamine

Chapter-1

Introduction

1.1 Nanoparticles

1.1.1 Overview

Nano is a prefix like milli, pico, micro and so on. Nano means one billionth, or 10^{-9} which is used in front of a macroscopic unit to change its value by orders of magnitude.[1] The scale which represents different dimensions is illustrated in the Fig. 1.1 given below:

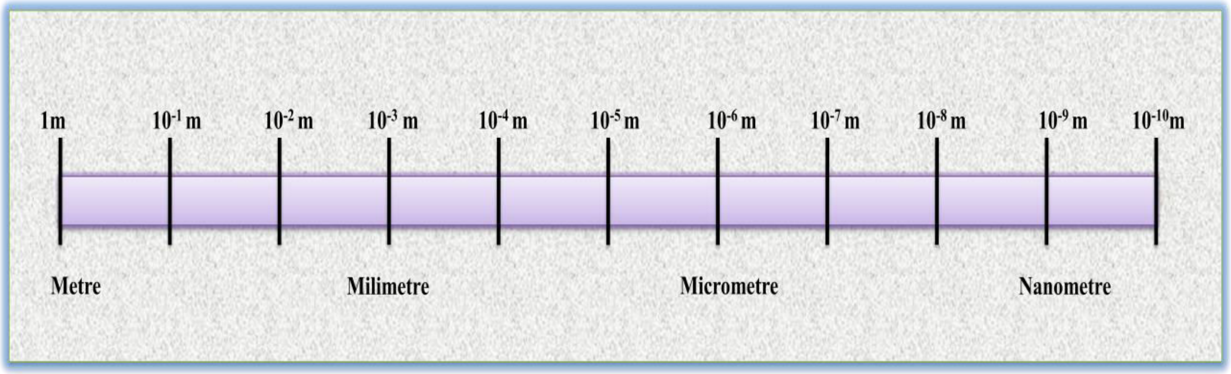


Fig. 1.1: A scale to represent different dimensions.

Nanotechnology is science, engineering, and technology conducted at the nano-scale, which is about 1 to 100 nanometers. This technology produces various types of materials at nano-scale level which are known as nano-materials. Nano-particles (NPs) include particular substances having dimensions below 100 nm from a wide class of materials.[2] This size range is generally associated with colloids, micelles, polymer molecules etc. NPs are link between atomic or molecular structure and bulk materials. On the basis of chemical and physical characteristics NPs are divided into many categories like carbon based NPs, metal NPs, semiconductor NPs, ceramics NPs, polymeric NPs and lipid based NPs, which depends on their size, chemical properties and morphology.[2] These materials are important as they do not obey laws of classical physics and absolute quantum chemistry due to their intermediate size. As the particle size reduces an increase in surface-to-volume ratio is observed and thereby catalytic activity and sensing property increases. On the basis of size their sensitivity varies NPs show sensitive properties towards the size of the particles, as the particle size increases, absorbance peak (λ_{max}) increases and broadens in width, zeta potential changes etc.[3] When the size of the particle is too small then specific effect is observed known as quantum size effect (QSE).[4] By varying band gap energy QSE, particles and designs with various properties can be synthesized.

1.1.2 Synthesis strategies

Mainly two routes are followed to synthesize NPs i.e. Bottom up approach and top-down approach. These approaches are further divided into subparts. As the name suggests in top down approach smaller units are obtained from larger molecules and thus these units are converted into NPs and in bottom-up approach larger units are obtained from smaller units and thus those larger units form NPs.[2] In bottom-up approach from atomic level materials are synthesized while in top-down approach materials are synthesized by bulk materials by reducing their size. The main drawback of top-down approach is that in this approach smaller fragments or materials are formed which have extensive size distribution i.e. > 100 nm. So this approach is not suitable for the formation of uniformly shaped materials but this method is favored for the synthesis of nano-materials and thin-films > 100 nm. Whereas bottom-up approach is suitable for formation of uniformly shaped materials so this method is more specific for the preparation of nano-materials with lesser imperfections, fewer impurities and fine size distribution i.e. < 100 nm.[5] Schematic representation of both the approaches are illustrated in Fig. 1.2.

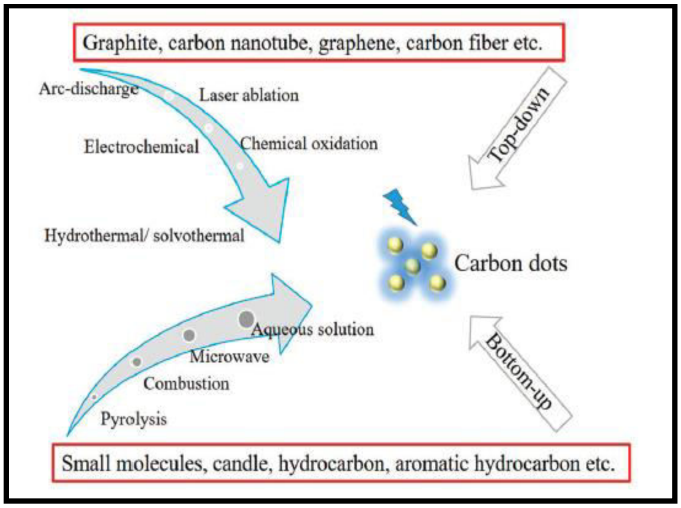


Fig. 1.2: Schematic representation of "top-down" and "bottom-up" approaches.

1.2 Carbon Quantum dots

1.2.1 Overview

Quantum dots (QDs) are semiconductor particles, just a few nanometers in a measure, so little that their optical and electronic properties vary from those of NPs. They are set up from atoms of group 2-6 or 3-5 in the modern periodic table. In comparison to bulk materials QDs have smaller excition Bohr radius (EBR). QDs are water-solubility, eco-friendly, have complex surface-chemistry and biocompatible. According to latest progresses QDs are presented for sensing and analysis, nano-drugs, syndrome monitoring and intercellular-imaging.[6] QDs are synthesized by heavy metals which are toxic in nature so a new member is introduced. In 2004 Xu *et al.* prepared carbon quantum dots (CQDs) from the most abundant material carbon while purify single-walled carbon nano-tubes (SWCNTs).[7] CQDs acts as potential competitors to normal semiconductor QDs they have comparable optical properties, even their fluorescence ability, simple synthetic routes, easy availability, biocompatibility and less toxicity make them superior w.r.t. QDs which have size range 2-10 nm with some form of surface passivation. CQDs are the NPs which belong from carbon nano-materials family having sizes < 10 nm. Several advancements were done in CQDs to improve their photoluminescence (PL) property through doping of different hetero-atoms, functionalization and utilization of different precursor and solvent system to obtain multicolored CQDs. Even to improve the sensing efficiency of CQDs chemical and physical mixtures of different CQDs and QDs were used to make calorimetric as well as fluorometric active nano-probe for the sustainable development. Chemical structure and three main classes of CQDs have been represented in Fig. 1.3 and table 1.1 respectively.

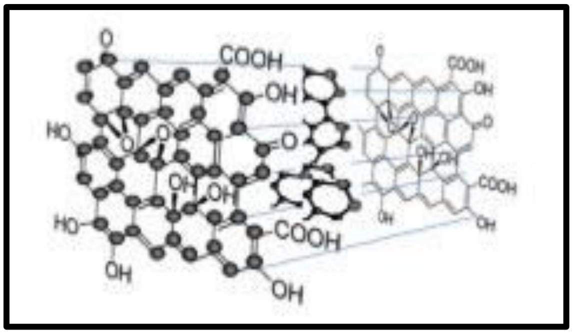
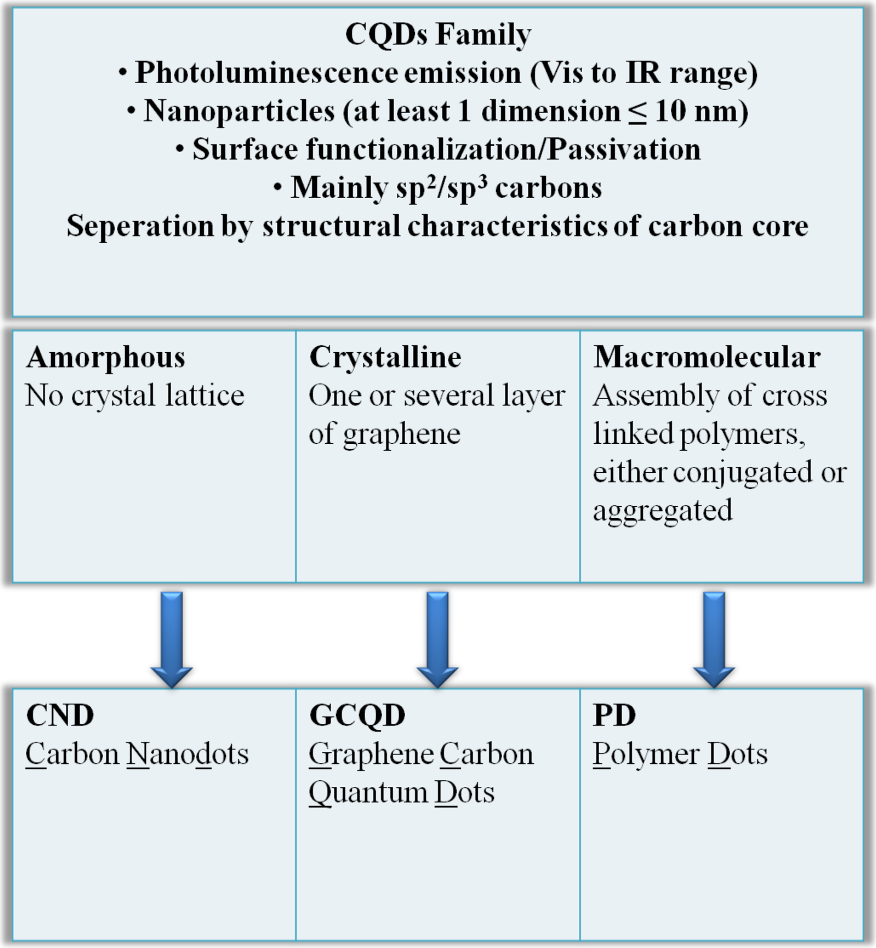


Fig. 1.3: Chemical structure of CQDs



CQDs Family
- **Photoluminescence emission (Vis to IR range)**
- **Nanoparticles (at least 1 dimension ≤ 10 nm)**
- **Surface functionalization/Passivation**
- **Mainly sp^2/sp^3 carbons**

Seperation by structural characteristics of carbon core

Amorphous	**Crystalline**	**Macromolecular**
No crystal lattice	One or several layer of graphene	Assembly of cross linked polymers, either conjugated or aggregated
CND Carbon Nanodots	**GCQD** Graphene Carbon Quantum Dots	**PD** Polymer Dots

Table 1.1: Schematic representation of the three main types of CQDs.

1.2.2 Synthetic routes

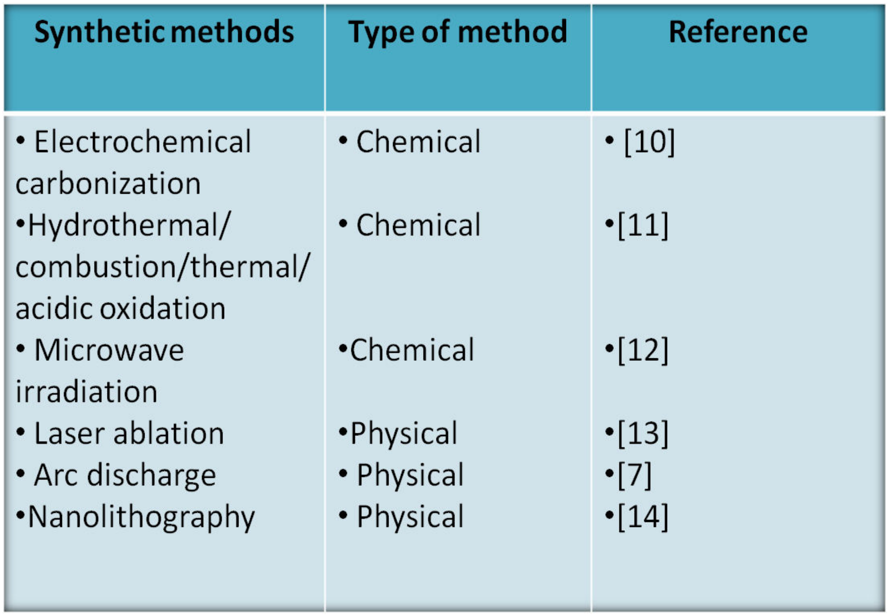
Generally there are two basic approaches for the synthesis of CQDs. Top-down approach for synthesis and Bottom-up approach for synthesis.

Top-down Approach

Several bulk carbon sources like carbon fiber, candle soot, fullerenes, activated carbon, graphite, graphene oxide, and carbon nano-tubes are fragmented to prepare photoluminicent CQDs. This can be achieved either by chemical routes or physical routes. Chemical routes involves electrochemical oxidation, hydrothermal oxidation method, solvothermal oxidation method or other unusual oxidation methods and metal-graphite intercalation.[8] Physical routes involves arc discharge, nanolithography and laser ablation.[9] As this approach is complex, sensitive towards environment and require highly toxic and expensive organic solvents “Bottom-up” approach is more favored for the synthesis of CQDs.

Bottom-up Approach

This approach is more flexible w.r.t “Top-down” approach as no specific molecular precursor is required. Starting materials can either be any carbonyl [CO], amino [NH_2], carboxylic [COOH], alcohol [OH] or their mixture for the synthesis of CQDs. various techniques can be used to obtain CQDs such as plain combustion, hydrothermal and microwave-assisted methods.[9] General synthetic methods are illustrated in Table 1.2.



Synthetic methods	Type of method	Reference
• Electrochemical carbonization	• Chemical	• [10]
•Hydrothermal/ combustion/thermal/ acidic oxidation	• Chemical	•[11]
• Microwave irradiation	•Chemical	•[12]
• Laser ablation	•Physical	•[13]
• Arc discharge	• Physical	•[7]
•Nanolithography	• Physical	•[14]

Table 1.2: Different synthetic methods for the preparation of CQDs

1.2.3 Properties of CQDs

Optical properties

Absorbance

Optical absorption is shown by CQDs in UV region mostly in range 250-320 nm with a tailing to the visible region. UV absorption peaks at different positions can be observed for CQDs prepared by different methods.[15] mainly two absorption bands appears due to n–π* transitions of C=O and π–π* transition of C=C.[16] In core carbon NPs π-Plasmon leads to the photo-excitation in CQDs. CQDs have relatively strong absorption due to the absorptivity values per molar concentration of carbon atoms in the core carbon NPs.[17]

Fluorescence

Radiative process for molecules when energy is absorbed by photons and then emitted from 1st excited singlet state (S_1) to the ground state (S_0) is called fluorescence. This is a slow process and have lifetime of 10^{-9} to 10^{-7} seconds.[18] This process in indicated by Jablonski diagram illustrated in Fig.1.4.

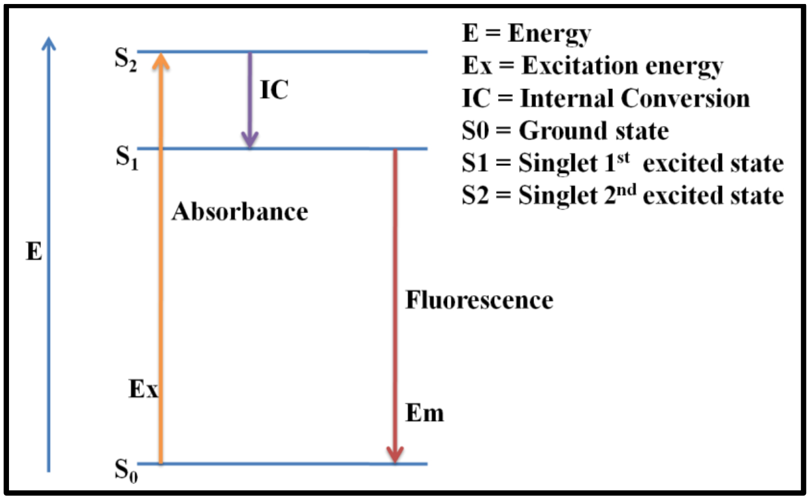


Fig. 1.4: Jablonski Diagram for fluorescence emission.

A very fascinating feature of CQDs, not only from elementary view point but also from application-oriented aspect is the photoluminescence (PL). CQDs have excitation-dependent (PL) emission property. This is due to the optical selection of the different sizes of NPs which is known as quantum effect or may be because CQDs surface have different emissive traps or due to some unresolved mechanisms.[19] Zhao *et al*. claimed that this property of CQDs is due to quantum effect more willingly than different emissive traps.[20] PL intensity of CQDs is pH dependent. When pH of CQDs solution is different from pH value 4.5 then PL intensity decreases and is totally recovered as it is adjusted back to its most favorable value. For the meantime, with variation in pH emission peak gets shifted. PL intensity of CQDs is completely quenched under strong alkaline or acidic conditions while at pH 7 strongest emissions are shown by CQDs. [21]

1.2.4 Applications

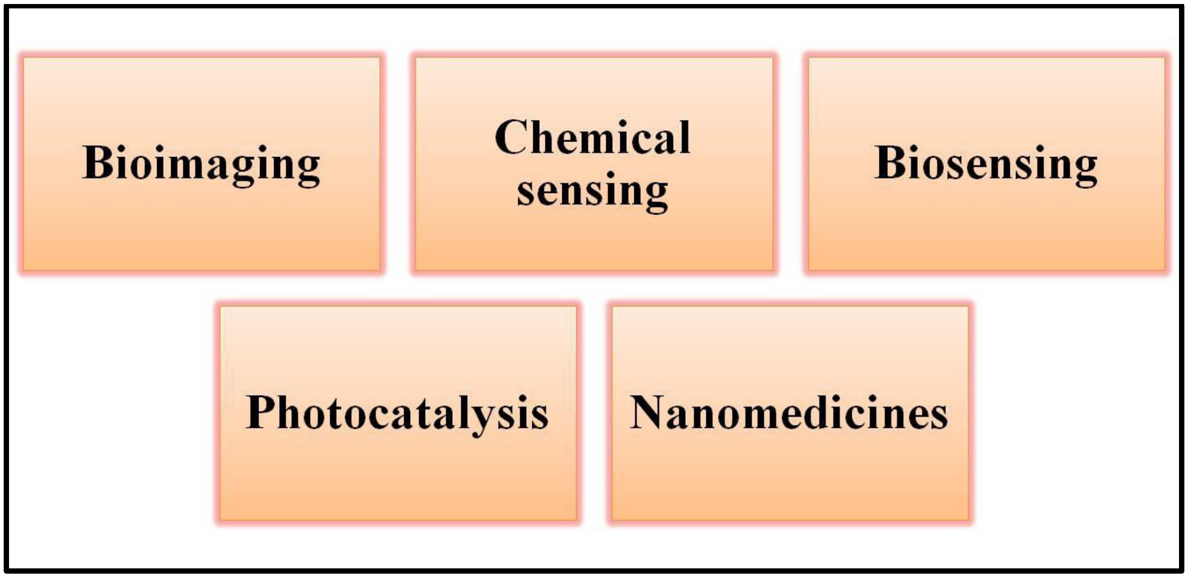


Fig. 1.5: Applications of CQDs

1. Bioimaging

Due to non-toxicity, photo-stability and optical properties, CQDs have several benefits in fluorescence imaging of cells. Also because of low surface charge and small size of CQDs there is low binding in cells.[22] Sun *et al*. and other research groups have investigated the application of CQDs in bio-imaging.[23] Coating of various functional groups onto the surface of CQDs and its approach for conjugating certain materials for surface modification via hydrogen bonds, covalent bonds and electrostatic interactions are highlighted. Also, the results from examination of multiple uses in sensing, high resolution bio-imaging and accurate drug delivery are highlighted.[24]

2. Sensing

CQDs coated with reactive group can thereafter be functionalized using highly specific detection elements. Many nano-materials have been synthesized as new nano-sensors in the field of bio/chemical analysis.[16] For instance, high sensitivity and selectivity of sensors for metal ions are generally made-up using conjugating chelating ligands as specific detection moieties onto the surface of CQDs whose fluorescence serves as a response signal.[24] An efficient strategy was built by Tian *et al*.[25] for sensitively and selectively sensing Cu^{2+} ions by covalently anchoring AE-TPEA on the surface of CQDs showing high sensitivity towards Cu^{2+}

with limit of detection 10 nM. Extensively CQDs are utilized for the detecting several chemical compounds, metal ions etc. This can be done under external chemical and physical conditions by analyzing the change in PL intensities. CQDs prepared by various methods are used for sensing purposes.[25] CQDs show better selectivity and sensitivity for sensing of metal ions which are biologically important. The functional groups which are on the surface of CQDs find a key role in the metal ion detection like Hg^{2+}, Cu^{2+}, Pb^{2+}, Fe^{3+}, etc. CQDs have been greatly subjected as biosensors for the detection of cellular copper, nucleic acids, glucose, Fe^{3+} etc due to high solubility of CQDs in water, surface modification flexibility, biocompatibility, high stability along with the interesting properties of exhibiting excitation dependent multicolor emission.[26]

4. Photo-catalysis

CQDs are not photo catalytic they have the application to enhance the property of photo-catalytic material. Over the couple of years, in organic synthesis photo-catalysis has paying attention as greener substitutes. As sunlight is an efficient energy source, huge concern has been observed for the photo-catalyst processes. But, this affects the organic compounds poorly because short wavelength and UV of visible light have high energy. Because of the availability of light for the longer wavelength and the ability of exchanging energy with CQDs offers an amazing outlook for these to get used in photo catalysis.[9]

5. Nano-medicine

High performances of non-cytotoxicity, high QYs and tunable fluorescence emission of CQDs, due to which they have been employed as drug delivery vectors and tracers. For example, Oxaliplatin with anticancer function was conjugated with amino capped CQDs via EDC/NHS amidation (Oxa–CQDs) which results in a brand new theranostic nano-medicine with various functions, such as multicolor bio-imaging, controlled drug release and a drug carrier. By monitoring the fluorescence intensity of Oxa–CQDs can be monitored, the track or distribute the drug molecule. Great potential applications of Oxa-CQDs in cancer diagnostics and therapy have been suggested by in-vio results.[27] CQDs are gentle for animals due to this they are considered in nano-medicines, so for functioning the studies in vivo they are well exploited.[9] This has been confirmed by in-vivo cyto-toxicity studies in mice, observations for this were done after a month of injecting mice with CQDs. It is observed there is no effect or damage on any of the internal functions and organs.[9]

Chapter 2

Literature review

Among different prominent forms of carbon, CQDs have come across as a new category of multicolor luminescent carbon nano-particles. These have drawn attention owing to their abundance, benevolence and inexpensive nature. A lot of attention has been received by CQDs in comparison to heavy metal based semiconductors, because of their extraoridanry PL activity, small size, non-toxic nature, biocompatibility, and brilliant photo stability towards photo blinking and bleaching. These distinctive characteristics make them interesting aspirants for a complete spectrum of advanced applications such as Bio-imaging and bio-labeling, environmental restoration, fluorescence, and photo-catalysis. Considering the potential and high relevance of CQDs, they have a bright future. Study of physiochemical properties, fabrication methods and applications of CQDs in various fields become important. In the research field, a number of approaches for preparation of the CQDs, their properties and prospective uses in sensing, photo-catalysis, bio-imaging have been reported.

In 2004 Xu *et al.*[7] prepared CQDs from the most abundant material carbon during purification of SWCNTs which were derived from arc-discharge soot. In this investigation, from the crude soot, mixture of fluorescent NPs, tubular and short components were the two new isolated classes of nano-materials.

In 2006, Sun *et al.*[28] prepared graphene nano-dots by oxidation-passivation technique by using carbon soot with PEG-1500N. They observed the passivated operator was essential to increase the fluorescence of CQDs.

In 2007, Liu *et al.*[29] prepared water soluble CNPs from the combustion soot of candles and their preparation, purification and characterization was also reported. Size of CNPs was very small (< 2 nm). CQDs prepared from this method have PL quamtum yield of 0.8-1.9%.

In 2007, Zhou *et al.*[10] synthesized CQDs using multi-walled carbon nano-tubes, acetonitrile, silver/per-chlorate as the reference electrode and tetra-butyl ammonium per-chlorate as the supporting electrolyte. Working electrode was treated by cyclic voltammetry. Prepared CQDs have Particle size 2.8 nm and PL QY 6.4%.

In 2007, Cao *et al.*[30] synthesized CQDs by laser ablation method using PPEI-EI technique, which were reported for cell imaging application.

In 2009, Zhu *et al.*[12] synthesized highly luminescent amorphous CQDs for the first time by using organisilane as a coordinating solvent with QY 47% in one minute.

In 2009, Yang *et al.*[13] synthesized fluorescent CQDs in which ^{13}C powder was used as carbon source with a PL QY of 20% .

In 2009, Yang *et al.*[31] prepared CQDs with different fluorescence emission wavelengths by combining passivation and laser ablation in one step using organic solvents with different surface coatings with low yield, which limits many potential applications. These CQDs have an average size and lattice spacing similar to diamond.

In 2010, Zhang *et al.*[32] synthesized fluorescent CQDs by a simple hydrothermal technique using ascorbic acid as a precursor with higher PL efficiencies 6.79%.

In 2011, Liu *et al.*[33] synthesized graphitized CQDs by a simple hydrothermal process using cetyl trimethyl ammonium (CTAB) as a precursor and nitric acid as surface oxidant. It has been observed that through surface esterification with glycol, PL QY (QY) could be greatly enhanced i.e. 10% and also due to the increase of the rigidity or coplanarity, PL of CQDs was enhanced.

In 2012, Peng *et al.*[34] synthesized GQDs of size range 1-4 nm which shows 2-D morphology by acidification and chemical exfoliation of carbon fibers. GCQDs with different size distribution were formed, because of the aggregated graphitic layers are broken. GQDs were demonstrated to be excellent probes for high bio-sensing and bioimaging applications.

In 2012, Zhou *et al.*[35] synthesized CQDs by pyrolysis of ethylene diamine tetra acetate which was used as a fluorescence sensor for the detection of biothiols and Hg^{+2} with high selectivity and sensitivity.

In 2014, Shen *et al.*[36] synthesized fluorescent CQDs by hydrothermal carbonization method using phenyl-boronic acid as a precursor which was used in non-enzymatic blood glucose sensing application.

In 2014, Dai *et al.*[37] constructed a fluorescence resonance energy transfer (FRET) system between gold nano-particles (AuNPs) and amino-functionalized CQDs by treating CQDs as energy donors and AuNPs as energy acceptors. Factors affecting FRET system were optimized for the detection of melamine on the basis of fluorescence intensity of CQDs. Linear relationship was obtained with a detection limit of 36 nM.

In 2016, Huang *et al.*[38] synthesized a single dual emissive (blue to red colour variation) nano-fluorophore probe to estimate blood glucose. The ratiometric fluorescence intensity of blue CQDs to red QDs is controlled.

In 2016, Xu *et al.*[39] synthesized hybrid (Eu^{3+}/CDs@MOF-253) using metal organic frameworks (MOFs), which was highly fluorescent in nature and showed dual-emissive behaviour. These were used as fluorescent probes for Hg^{+2}detection.

2.1 Research gap

- Till now only single emissive CQDs/CQDs@QDs were used for the detection of metal ions/bio-molecules.
- There is very little work done on the synthesis of dual emissive CQDs using single precursor using hydrothermal method.[40] There is no literature report of dual emissive CQDs using microwave assisted method.
- A Solvatochromic study with dual emissive CQDs is not done yet
- There is not much significant work carried out to quantify metal ions/bio-molecules using dual-emissive CQDs.

2.2 Aim of project

- Synthesis of dual-emissive CQDs using carbohydrates with mixture of acids.
- Effect of polar solvents (protic and aprotic) on PL properties of dual-emissive CQDs.
- Implementation of dual-emissive CQDs for the detection of metal ions/melamine based on turn-on/-off PL methodology.

Chapter 3

Methodology

3.1 Materials and Reagents

Reagents of analytical reagent grade were used without any advanced refinement. Sucrose purchased from Qualikems was used as a starting precursor without any purification. Ortho-phosphoric acid purchased from Lobachemie and Sulphuric acid purchased from Rankem were used in the synthesis of CQDs. Ferric nitrate (nonhydrate) purchased from Lobachemie was used for metal ion detection. Melamine purchased from TCI was used for biomolecule sensing. Methanol HPLC purchased from SDFCL, DMF purchased from Merck and Acetonitrile purchased from Spectrochem were used for solvent studies. Aqua regia was used for cleaning of glass wares. Ultrapure deionized water obtained from Millipore (Resistance: 18 MΏ, 25°C) was used for the preparation of all reagents and cleaning of glass wares.

3.2 Synthesis of CQDs

Water soluble CQDs were synthesized by dissolving 0.5 g sucrose (0.15 M), 200 µL Ortho-phosphoric acid and 100 µL Sulphuric acid in 10 mL water with continuous stirring. After 10 minutes, the sample (10 mL) was transferred into a glass reaction vessel and subjected to microwave heating at 130^{o}C for 10 minutes at 300W power with a Multiwave-3000 microwave reaction system (Anton Paar, USA). The formation of CQDs was confirmed with the change in the colour of sample from colourless to brown. Then the solution was centrifuged for purification at 5000 r.p.m for 30 min to collect pure CQDs. The scheme for the synthesis of CQDs has been illustrated in Fig. 3.1.

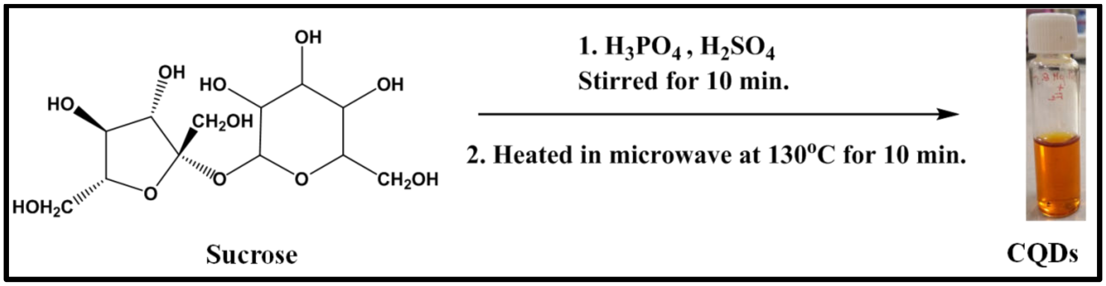


Fig.3.1: Scheme for the synthesis of CQDs

3.3 Instrumentation

Optical properties of CQDs was analysed using following techniques: UV-Vis spectrophotometer (SHIMADZU UV-2600, India) and fluorescence spectrophotometer (PerkinElmer LS-55, USA) using an excitation wavelength 350 nm. The morphology and particle size of CQDs were determined by the transmission electron microscope (TEM). Attenuated total reflectance infrared spectroscopy (AT-IR) was recorded to know the different functional groups on the surface of CQDs by using Agilent Resolution Pro-carry 660.

3.4 Detection Procedure

3.4.1 Detection of metal ions

Prepared CQDs were used for metal ion sensing, the desired volume (100 µL) of CQDs from its stock solution was diluted to 2 mL using polar solvents (H_2O, MeOH, DMF and ACN) in the quartz cell. Then, the suitable volumes of Stock solution (0.001M) for different metal ions was prepared using metal salts like ferric nitrate, copper nitrate, nickel nitrate, and mercury chloride to study their interaction with CQDs were added into the quartz cell gradually by using a micropipette to generate the metal-ion-mediated CQDs fluorescence probes. Fluorescence data were recorded at 5 min. after the addition of the metal ions. The excitation wavelength was fixed at 350 nm and emission spectra were recorded.

3.4.2 Detection of melamine on the basis of Turn-off/-on fluorescence of CQDs

The typical assay procedure was as follows: specific volume of $Fe(NO_3)_3.9H_2O$ solution (0.001M) was mixed with 100 µL of CQDs solution diluted with 2 mL of polar solvents. Then, suitable volume of melamine stock solution (0.001M) was added. After 5 min, the PL spectra of mixture were recorded at excitation wavelength 350 nm.

Chapter 4

Results & Discussion

4.1 Characteristics of CQDs

The prepared CQDs were characterized by HRTEM, AT-IR, and fluorescence spectrometry. Firstly, the formation of dual-emissive CQDs was confirmed from its dark yellow colour suspension, yellow and green fluorescence under UV lamp at long UV range and short UV range respectively. PL spectra of CQDs was observed (λ_{em} =350 nm) shown in Fig. 4.1. The HR-TEM images demonstrate that CQDs were partially mono-dispersed and spherical. The average diameters of CQDs in the presence of sulphuric acid and ortho-phosphoric acid were 2 ± 0.5 nm and 6 ± 2 nm respectively, which is shown in Fig. 4.2. The AT-IR spectrum of CQDs exhibits absorption peak at 3347 cm^{-1} (O-H stretching), 1744.5 cm^{-1}(O-H bending), 1638.5 cm^{-1} (C=O group), and 1512 cm^{-1} (C=C stretching of aromatic compounds) which confirmed that different functional moieties are present on the surface of CQDs (Fig. 4.3).

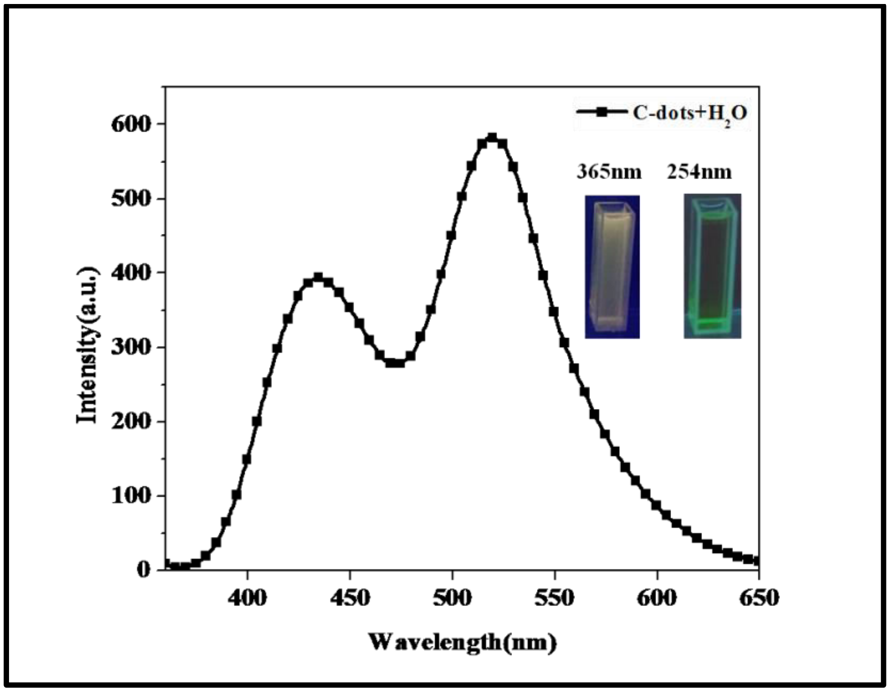


Fig. 4.1: PL spectra of dual-emissive CQDs.

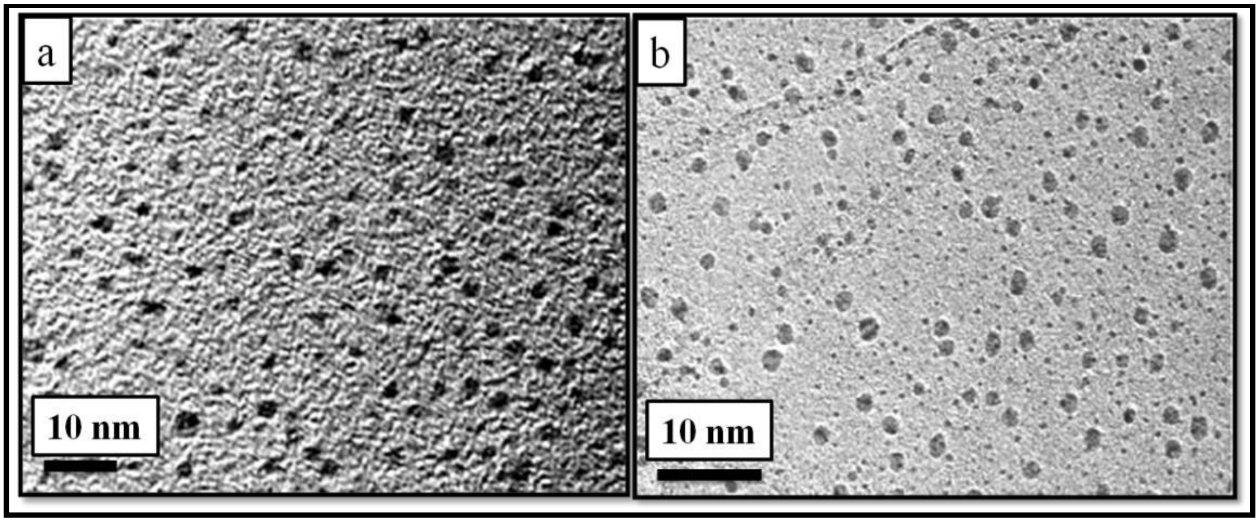


Fig. 4.2: HR-TEM images of CQDs

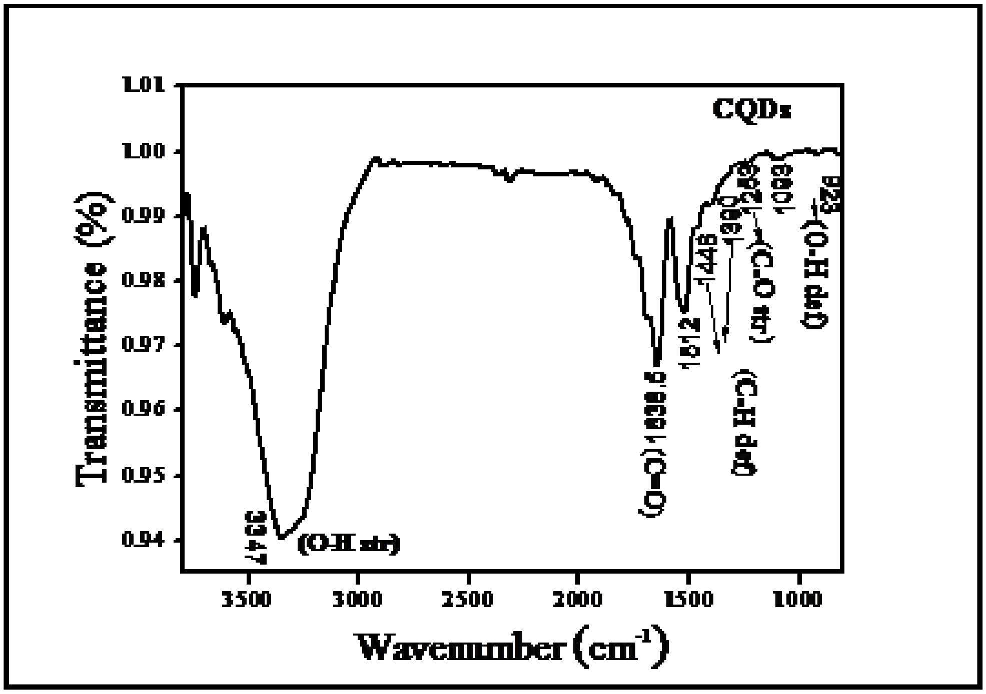


Fig.4.3: AT-IR of CQDs

4.2 Optimization of reaction conditions for the detection of metal ions

The efficiency of the fluorescent probe depends on numerous parameters such as pH, excitation wavelength and a slit width of fluorescence spectroscopy. So, to enhance the sensitivity and selectivity of the sensing probe, there is a requirement to optimize the reaction conditions. Here, different excitation wavelength and slit width were used to access the variation in its PL intensity. It was found that, CQDs with slit width 10 nm and 18 nm, exhibited maximum PL intensity (Fig. 4.4(a)).The effect of pH was also recorded for the CQDs on its PL intensity (Fig. 4.4(b)). The results demonstrated that mild acidic condition was suitable for performing PL quenching and recovery experiment. Whereas, highly acidic and basic condition found inappropriate due to protonation of carboxylic groups and formation of $Fe(OH)_3$,[41,42] which result in weaker interaction of CQDs with Fe^{3+} ions and reduction in its sensing efficiency.

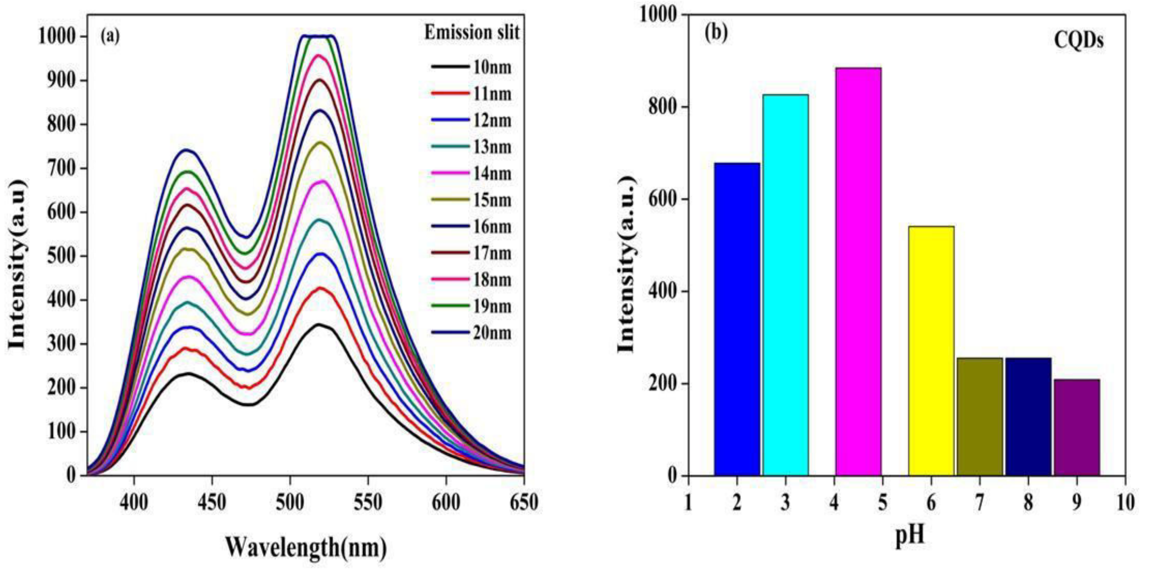


Fig.4.4: Optimization of experimental conditions: (a) effect of emission slit width at constant excitation slit width, and (b) effect of pH on the fluorescence intensity at λ_{ex}= 350 nm for CQDs.

4.3 Selectivity of CQDs towards different cations

Selectivity is a vital parameter to evaluate the performance of chemo-sensor. So, the interaction of CQDs was examined with different metal ions (e.g. Fe^{3+}, Cu^{2+}, Zn^{2+}, Mg^{2+}, Pb^{2+}, Fe^{2+} and Ni^{2+}) by estimating the variation in its PL intensity. The experimental results revealed that Fe^{3+} ions exhibited maximum fluorescence quenching for CQDs (~63%) due to strong interaction with carboxylic/hydroxyl groups on the surface of CQDs (Fig. 4.6). This quenching mechanism was explained on the basis of hard-soft-acid–base (HSAB) principle. Fe^{3+} was used to perform recovery experiment (turn-on) with melamine.

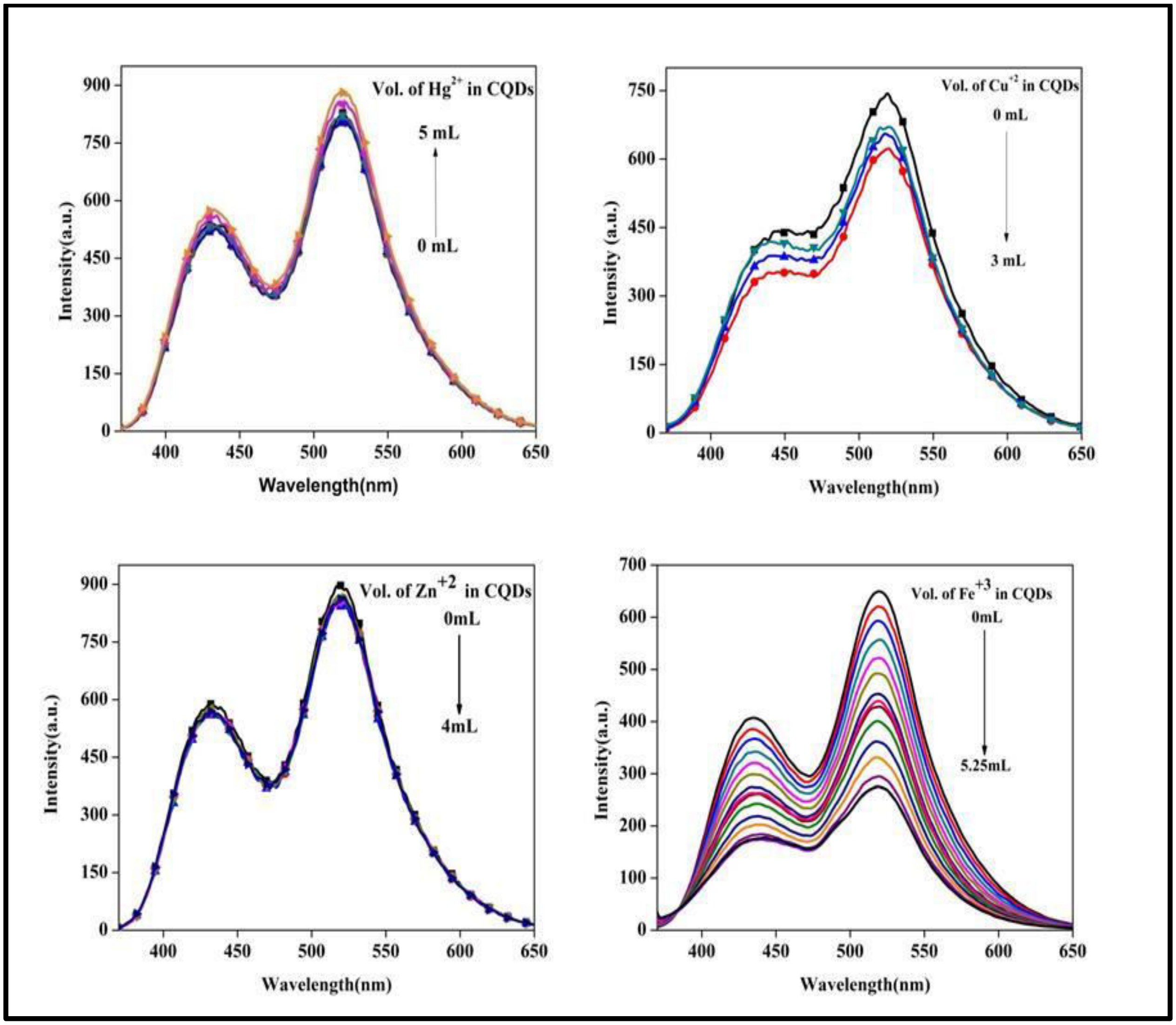


Fig. 4.5: Fluorescence quenching spectra of CQDs in the presence of different ions.

4.4 Solvatochromic effect on CQDs

On dispersing dual emissive CQDs in different solvents, spectral shifts accompanied by a change in their intensities were observed. To elucidate the effect of solvatochromic shift on the PL of CQDs, fluorescence emission was carried out in presence of different polar protic and polar aprotic solvents illustrated in Fig.4.6. In DMF (polar aprotic solvent), red shift and hyperchromic shift has been observed. In ACN (polar aprotic solvent), red shift and hypsochromic shift were also observed. In MeOH (polar protic solvent), red shift and hypsochromic shift has been observed. In general, solvatochromic shifts in presence of CQDs are due to hydrogen bonding interactions and dipole-dipole between the solute-solvent (CQDs are regarded as solute particle) model system. There are several kinds of solvatochromic model systems such as Lippert Mataga (LM) model,[43] Kamlet Taft (KT) model, Dimroth model, Catalan 3P and Catalan 4P model and so on. LM model explained that solvent molecule with a specific dielectric constant value can stabilize the electronic states of the CQDs which is fluorescent in nature. But, for such a stabilization of the CQDs, it is necessary for the fluorophore to reorient around the solvent molecule before emission. This will be possible when the solvent relaxation takes place prior to emission.[44] The stability of the ground state as well as excited state of the CQDs in different solvents is mainly gained by the electron transfer from its various functional moieties of CQDs to the respective neat solvents. For that reason, because of the stabilization of the ground state and excited state, CQDs showed red shift in the PL spectra. The higher value of red shift occurs, where the dielectric constant value (ε) will higher as proposed by Lippert and Mataga. In case of non-polar solvents, the reorientation polarizability is negligible. Therefore, solvate-chromic model system is applicable in polar protic and aprotic solvents only. Kamlet-Taft (KT) model explained the hydrogen bonding interactions between the solute and solvent molecule. Three parameters such as α, β, and π* indicates the KT model. These parameters indicate that the solvent molecule has hydrogen bond donating (α) ability (HBD), hydrogen bond accepting (β) ability (HBA) and solvents polarizability (π*). In other words, KT model describes the hydrogen bond interaction behavior of solute-solvent system. [45] The values of the above mentioned parameters for the chosen polar solvents are listed in Table 4.1.

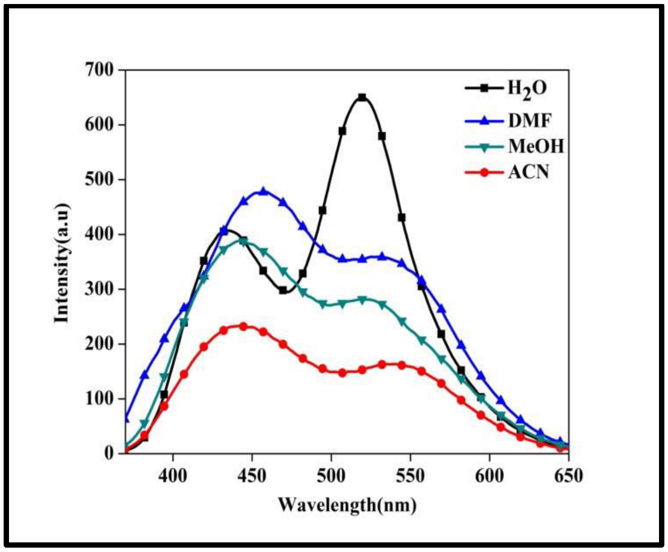


Fig. 4.6: CQDs with various solvents.

Solvent System	**Type**	**Lippert parameter**	**KT model parameter**			**Dielectric constant**
		Δf	π^*	α	β	
H_2O	Polar protic	0.320	1.09	1.17	0.18	80
MeOH	Polar protic	0.310	0.60	0.93	0.62	32.6
DMF	Polar aprotic	0.275	0.275	0.88	0.69	36.7
ACN	Polar aprotic	0.305	0.75	0.19	0.31	36.64

Table 4.1: List of values of Lippert parameter, KT parameters and dielectric constants for various solvents.[45]

4.5 Turn-off/-on mechanism

The variation in PL intensity was studied for the foundation of conceivable sensing mechanism of the probe. To determine the sensing mechanism initially, the variation in PL intensity was estimated for CQDs and ferric ion sensor system. It was found that in the presence of ferric ions, the PL intensity was recovered for the CQDs (Fig. 4.7). Gradual increase in the PL intensity of dual emissive CQDs was observed with increasing concentration of melamine, which indicates that the presence of melamine can effectively coordinate with Fe^{3+}, preventing the fluorescence quenching process induced by Fe^{3+}, because of multi-nitrogen heterocyclic ring of melamine, strong and special coordination affinity to Fe^{3+} produces the fluorescence recovery of CQDs-Fe^{3+} system.[46] From Fig. 4.7(a), it can be seen that this proposed method exhibited good behavior to the determination of melamine process. To calculate the detecting limit of the probe, The plot between fluorescence enhancements, F/F_0 against concentration was done shown in Fig. 4.7(b). The equation of the linear fitted curve, $F/F_0 = 6.25[\text{Melamine}] + 0.917$ helped in determining the detection limit which was found 0.02µM and regression coefficient was 0.936.

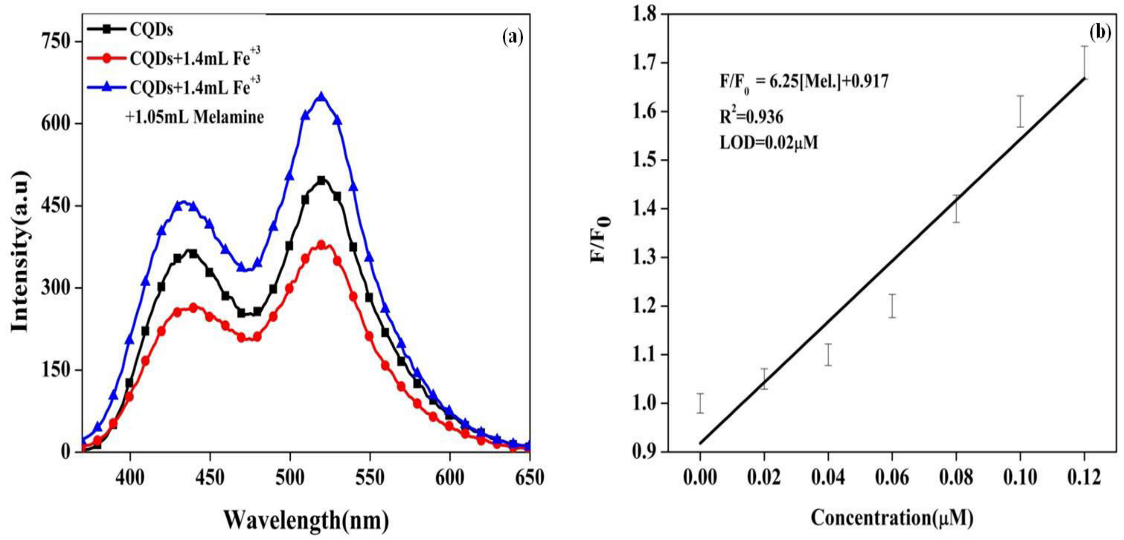


Fig. 4.7: (a) Sensitivity of CQDs towards melamine in the presence of Fe^{3+} ions and (b) Plot of PL intensity variation at λ_{em}=350 nm as a function of concentration of Melamine for the quantitative determination of Melamine.

Chapter 5

Conclusion

This thesis introduces the synthesis of dual fluorescence emission CQDs by using microwave synthetic route to carbonize sucrose using two different acids, H_2SO_4 and H_3PO_4. The synthesized CQDs are characterized by HR-TEM, AT-IR techniques. Solvatochromic effects were studied, due to the different nature of functional groups present on the surface of synthesized CQDs and their complex interchange with solvents. PL shifts were observed which were examined thoroughly on the basis of Lippert Mataga and Kamlet Taft model. On the basis of these models, interaction of different polar solvent with CQDs can be justified. Various metal ions were used to study the effect on PL intensity of CQDs. Ferric ions were found to be more selective for quenching. A simplistic turn-on fluorescence detection method for melamine based on CQDs was developed. This approach relies on anti-quenching ability of the Fe^{3+} ions to fluorescent CQDs through the coordination of melamine with Fe^{3+} ions. The mixture of CQDs and Fe^{3+} ions shows sensitivity towards melamine with a LOD of 0.02 µM. The nano-probe has a good potential for ecological and environmental safety.

Chapter 6

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