Tetracycline Conjugated Quantum Dots for Simultaneous Imaging and Antibacterial Therapy

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Abstract: Quantum dots (QDs) are a landmark development in the field of nanotechnology. These zero-dimensional semiconductors, unlike their physical attributes, have enormous capacity to store energy within themselves. This is contained in several thousand electrons that constitute the nanoparticles. Quantum dots excel at a myriad pf physical properties, most notably their fluorescent properties, such as high quantum yield, photo-stability, broad absorption spectra, and their remarkable size-dependent emission-tunability. QDs can absorb and re-emit the incoming radiation in the desired direction with the tunable spectrum, which renders them favorable for building integration. There are host of potential applications for QDs including solar cells, LEDs, medical imaging, biosensing, single electron transistors, and a host of other electronic products. The synthesis of tetracycline QDs typically involves surface functionalization of QDs followed by covalent or non-covalent attachment of tetracycline molecules. These conjugated systems exhibit excellent fluorescence properties, enabling their application in bioimaging, targeted drug delivery, and bacterial detection. Overall, tetracycline-conjugated quantum dots provide a multifunctional platform that integrates diagnosis and therapy, offering significant potential in biomedical research, especially in infection imaging and targeted antimicrobial treatment.

Keywords: QDs, Core-type QDs, Nanotechnology, nanomedicine, nanoparticle, Bionanotechnology, Targeted Therapy, Semiconductor Nanocrystals.

I.INTRODUCTION

Quantum Dots (QD) are highly crystalline molecular sized semiconductor nanocrystals (2-10 nm). These are made up of 100-1000 atoms.[1] “Quantum” is a Latin word which means minimum amount of any physical entity involved in an interaction.[4] Tetracycline (TC) are broad-spectrum antibiotics widely used in aquaculture and animal husbandry to inhibit various bacteria and treat diseases.[2] In 1981, Alexey Ekimov (in glass) and Louis Brus (in solution) independently observed quantum size effect in nanocrystals. These were the first quantum dots.[3] These can be thought of as a 3D quantum well constrained to zero dimensions. QD’s when excited to higher energy levels relax radiatively by emitting a characteristic photon and coming to the ground state energy.[5] In 2023 Nobel Prize in Chemistry was awarded to Aleksey I. Ekimov, Louis E. Brus, and Moungi G. Bawendi for groundbreaking inventions in the field of nanotechnology ,i.e., for synthesis of semiconductor nanocrystals, also termed quantum dots, that exhibit size-dependent physiochemical properties enable by quantum size effects.[6] They are used extensively as fluorophores in many type of fluorescence sensing; in imaging, phototherapy, and optoelectronic device; and as catalysts in biochemical and chemical reactions.[7]

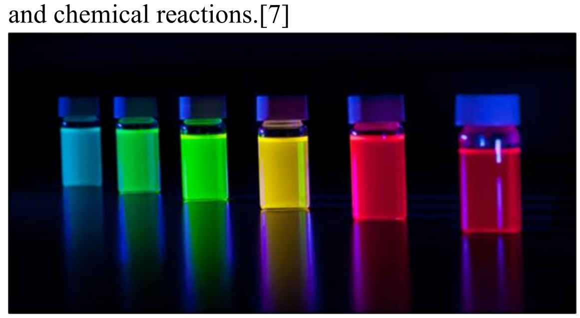

Figure No.1: Photoluminescence of QDs

II.CLASSIFICATION OF QUANTUM DOTS

Quantum dots are classified into various types based on composition, structure, type of material used, type of technique used for synthesis.[8]

Three basic categories are used to categorize quantum dots:

- Based on their composition and structure
- Based on the material used
- Based on technique to synthesis

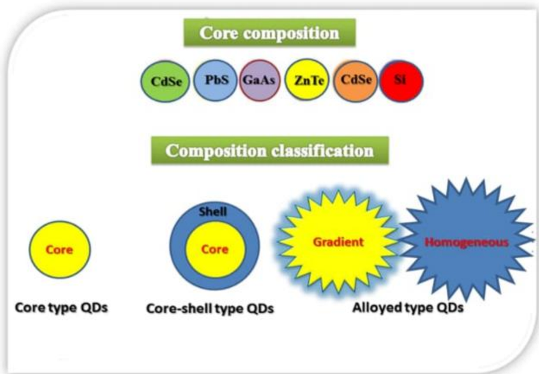

Figure No. 2: Classification of quantum dots based on their composition and structure

1. Based on their composition and structure

- Core-type quantum dots:
  Core- type quantum dots are predominantly made of single substances, often metallic chalcogenides such as cadmium telluride (CdTe) or lead sulfide (PbS). These nanocrystals generally range from 2 to 10 nanometer in diameter, allowing quantum confinement effects that drastically modify their electrical and optical characteristics compared to bulk material. It is a simple structure but may have lower stability. Core-type QDs may emit vivid and pure colors, with the capacity to generate a variety of colors depending on their size. Smaller dots produce light at shorter wavelengths (blue), whereas bigger dots emit longer wavelength (red) owing to changes in energy levels.[9]

- Core-shell type quantum dots:
  Core-shell QDs consist of a semiconductor core surrounded by a shell of another semiconductor material. This design enhances stability and photoluminescence efficiency by sheltering the core from oxidation and degradation. The production techniques often include high-temperature reactions or aqueous procedures that allow for fine control over the size and content of the QDs, which in turn determines their optical properties. Core-shell QDs have strong emission peaks, making them appropriate for applications needing accurate color outputs. They absorb greater spectrum of light, boosting their value in applications like photovoltaics and bio-imaging.[10]

- Alloyed type quantum dots:
  Alloyed QDs are often manufactured by high-temperature procedures or wet-chemical processes, allowing for exact control over their size and composition. The synthesis procedures may greatly impact on the resultant QDs' features, particularly their optical qualities and stability. Common materials used in alloyed QDs include mixtures of II-VI and III-V semiconductors, such as CdSe (cadmium selenium), ZnS (Zinc Sulphur), and InP (indium-phosphide). Alloying may lower non-radiative recombination losses, resulting in greater photoluminescence quantum yields.[11]

2. Based on the material used

- Silicon-based quantum dots:
  Silicon quantum dots (SiQDs) are nanoscale semiconductor particles composed mostly of silicon, generally ranging from 1 to 10 nanometers in size. These quantum dots display unusual optical and electrical features owing to quantum confinement forces. The photoluminescence of SiQDs may be modulated throughout the visible spectrum to near infrared by altering their size. Smaller dots tend to produce shorter wavelengths (blue light), whereas bigger ones emit longer wavelengths (red light).[12]

- Perovskite quantum dots:
  Perovskite quantum dots (PQDs) are a family of nanomaterials defined by their unique crystal structure and exceptional optoelectronic capabilities. The band gap of PQDs may be changed by modifying their size and composition, allowing for emission throughout the whole visible spectrum. PQDs may reach photoluminescence quantum yield of 80% making them very efficient light emitters.[13]

- Carbon quantum dots:
  Carbon quantum dots (CQDs) have attracted great attention because of their distinctive structural dimensions, as well as their outstanding chemical and physical properties. CQDs have attractive features such as ease of synthesis, good water solubility, high photostability, high photo response, low cytotoxicity, facile surface functionalization, good catalysis properties and tunable excitation emission.[14]

3. Based on technique to synthesis

- Colloidal quantum dots:
  The band gap of CQDs may be modified by modifying their size and composition, allowing for fine control over their absorption and emission wavelengths. CQDs may be manufactured utilizing numerous ways that allow for exact control over their size and contain such Hot-injection method, Solvothermal synthesis and Ligand- Assisted Reprecipitation. CQDs may reach photoluminescence quantum yields of 80%, making them efficient light emitters suited for display and lighting applications. They often display narrow Full Width at Half maximum (FWHM) values, which promotes color purity in applications like light-emitting diodes (LEDs).[15]

- Magnetic quantum dots: Magnetic quantum dots (MQDs) are nanoscale semiconductor particles that display unique magnetic characteristics alongside their quantum confinement effects. MQDs demonstrate superparamagnetic behavior, where they may become magnetized in the presence of an external magnetic field but do not sustain magnetization after the field is withdrawn. [16]

- Fluorescent quantum dots:
  Fluorescent quantum dots (FQDs) are nanocrystalline semiconductor particles that have received substantial interest in the domains of imaging, sensing, and therapies owing to their unique optical features. The emission wavelength may be carefully controlled by adjusting the size of the FQDs. This enables a broad spectrum of hues from blue to near-infrared, making them adaptable for multiplexing applications. [17]

III.METHODOLOGY

Many researchers have developed different preparation techniques for alloyed ternary quaternary quantum dots.

1. Hot injection method:

Although hot injection is widely used techniques for the preparation of quantum confined semiconductor nanoparticles with manifold application in the fields of energy, biology, telecommunication, and display technology, design rules for scalable processes for this complex kind of synthesis do not exist. Some QD synthesis routes at room temperature in aqueous solution do exist, hot injection which is focused in here involves the fast addition of a cold precursor (at -25· C) to a hot metal-organic precursor (typically at temperature >225· C), enabling the separation on nucleation growth processes. Thus, so-called monodisperse products with high crystallinity are obtained. It is also obvious that the production of such a high-quality product by hot injection requires high skilled experimentalists due to (i) high temperature gradients, (ii) sensitivity of QD synthesis against smallest changes in feed quality and reactant concentrations, (iii) fast kinetics, (iv) demanding requirements in terms of cleanliness and the (v) additional need to exclude oxygen and humidity. [18]

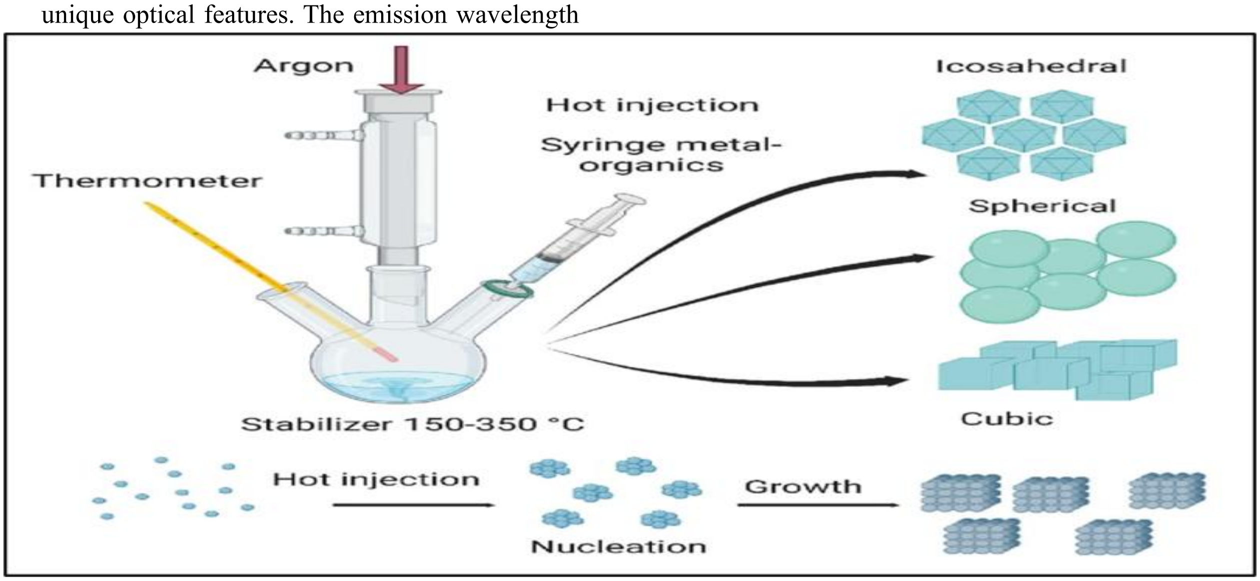

Figure No.3: Schematic representation of the hot injection synthesis of nanocrystals

2. Chemical oxidation method:

Chemical oxidation is the most common top-down route for preparing CQDs because of various advantages such as high yield, high purity, low cost, and reasonable control over the size. It is used to exfoliate and break down large chunks of carbon into small pieces while simultaneously adding hydrophilic groups like hydroxyl (-OH) or Carboxyl (-COOH) groups that could improve water dispersion and FL characteristics of the resulting particles. Oxidants such as HNO3, phosphoric acid (H3PO4), and sulfuric acid (H2SO4) are used to facilitate the carbonization of plant parts to get CDs. In most cases, the parts of the plant are first carbonized, combined with a chemical oxidant, followed by separation and purification operations. Thus, producing CQDs using the chemical oxidation approach is simple, scalable, and does not require expensive equipment. [19]

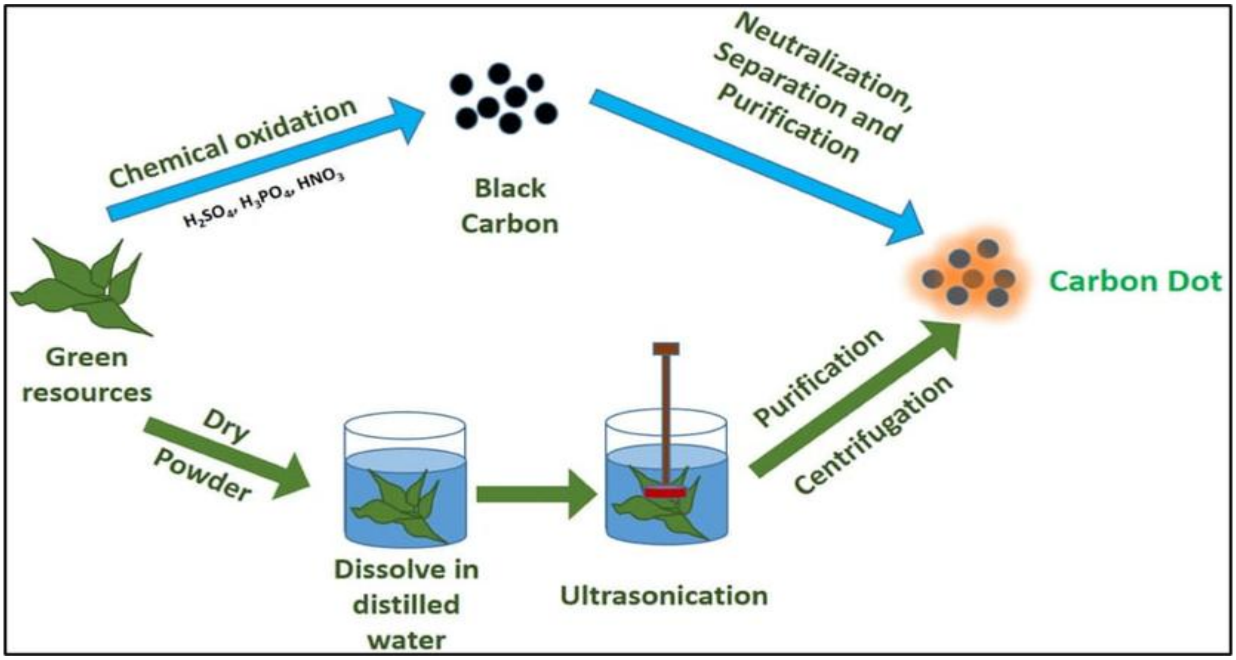

Figure No.4: Chemical oxidation preparation method for CQDs

3. Hydrothermal method:

The hydrothermal technique is an effective method to synthesize carbon dots from plant derived materials in an aqueous solution at increased pressure and temperature. Four essential processes are involved in this method mainly Carbonization, dehydration, passivation, and polymerization. To synthesize CDs of different composition, size, shape, and crystalline, several reaction parameters can be varied such as type of solvent, concentration, temperature, pressure, and reaction time. In this process, the precursor solution is kept inside a Teflon-lined autoclave chamber which is then subjected to high pressure and temperature above the solvent's boiling point to synthesize CDs. This procedure involves using water as a reaction medium in a sealed system while maintaining the temperature between 150 and 300·C and the pressure was maintained up to 2000 psi for 2-14 h. The key benefit of this method is to synthesis nanomaterials from different source without the need for any pre-treatment procedure. The advantages of this method include effectiveness and flexibility of synthesizing CDs with this method. [20]

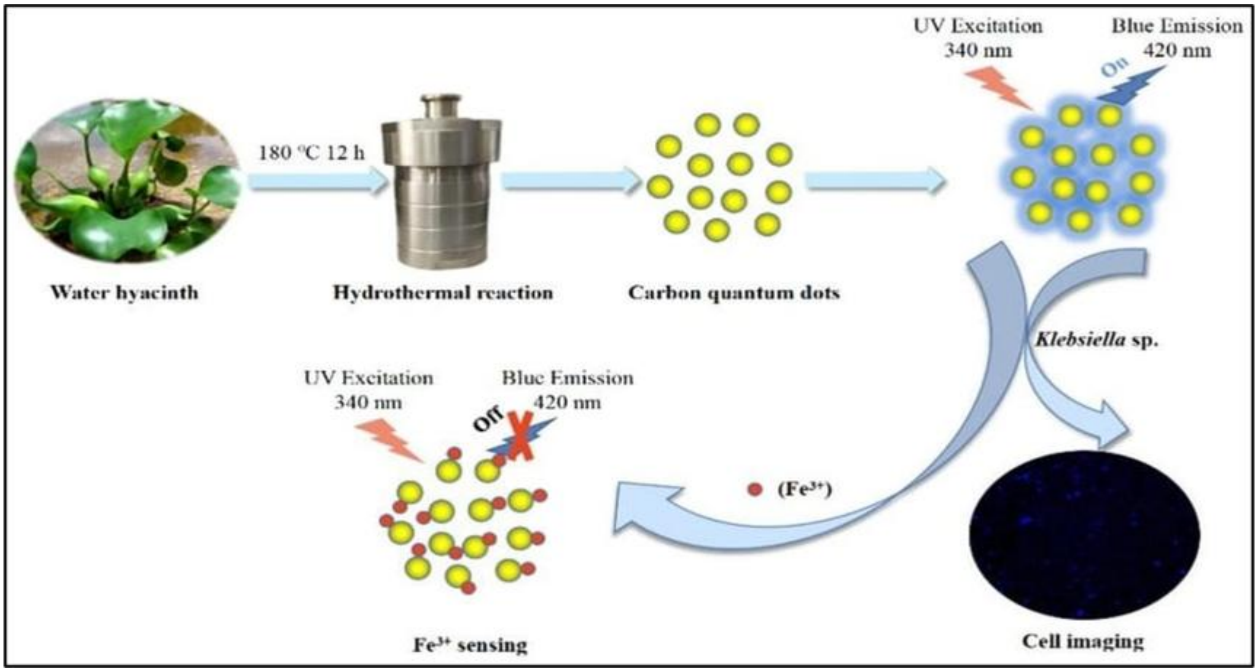

Figure No.5: Hydrothermal method for the preparation of CQDs.

4. Microwave-assisted Method:

The Microwave-assisted (MW) consists of synchronized perpendicular oscillations of electric and magnetic fields. This MW energy absorbed by carbon materials and transformed into the form of heat is called dielectric heating. MW-assisted synthesis is highly used in the field of carbon research as carbon materials interact strongly with MW radiation producing fast heating rates and localized heating. Thus, nanostructured carbon materials, metal oxide nanoparticles supported by graphene and metal oxide supported by carbon nanotubes (CNTs) have been obtained by MW-assisted synthesis. The MW-assisted synthesis is an effective method for QD preparation, and several reports confirm the feasibility and potential of this technique. The MW-assisted route is the most promising clean, low-temperature, and economic synthesis routes. One of the supreme and noteworthy advantages of this method, which constrains specific shape and size of QD dependence on the experimental parameters, is also brough to focus. The QDs synthesized by MW using either top-down or bottom-up approaches are broadly adopted for various research applications, including drug delivery, biosensors, bioimaging, fuel cells, supercapacitors, photocatalyst, photovoltaics. [21]

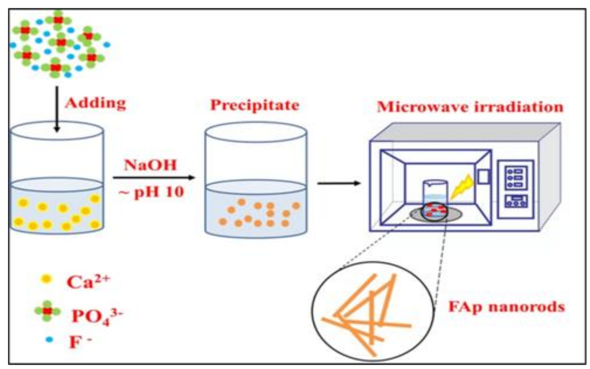

Figure No.6: Schematic illustration of microwave assisted synthesis of FAp nanoparticles.

Biological Applications of QDs

The numerous uses of quantum dots may be categorized under the following key headings:

1. As cellular probes. [22]
2. Fluorescence resonance energy transfer (FRET).[23]
3. Cell tracking and intracellular delivery (Immuno-labelling). [24]
4. Radio opacity and paramagnetic properties.
5. MRI contrast agent, it has been showing that QDs can be used for bio-imaging purposes.[25]
6. Tissue staining.
7. Gene delivery.[26]
8. Cellular imaging.[27]

9. Cellular motility assays.[28]

Experimental Section

Materials

Sr. No.	Ingredients/Chemicals	Quantity
1	Chenpi	0.1 g
2	Ethylene glycol	10 ml
3	Tetracycline	o.5 g

Table No.1: List of Ingredients used in Preparation

- *Chenpi:* Dried citrus peel (*chenpi*) is the mature dry pericarp of Citrus reticulata. As a good traditional Chinese medicine. It contains many active components, such as essential oils, flavonoid, pectin, insoluble fiber, and so on. Citrus peel essential oil may ameliorate hypercholesterolemia and hepatic steatosis by modulating lipid and cholesterol homeostasis, and most of them have good antimicrobial and antioxidant activities. [29] It can be collected in the form of dried powder from Pharmacognosy department of Rashtriya College of Pharmacy, Chht. Sambhajinagar.

Figure No.7: Dry *Chenpi*

Drying and Powder Preparation

1. Wash Citrus Peel
2. Dry them in Sunlight for several days
3. Grind *Chenpi*
4. Pass powder through Sieve no. 80 to obtain fine powder
5. Store in airtight container

- Ethylene glycol: Ethylene glycol ($C_2H_6O_2$) is highly utilized in quantum dot (QD) formulation, primarily as a versatile solvent, reducing agent and reaction medium for polyol synthesis. It is a clear, odorless, and sweet-tasting syrup liquid. It can be collected and issue from the Department of Pharmaceutical-Chemistry of Rashtriya College of Pharmacy, Chht. Sambhajinagar.

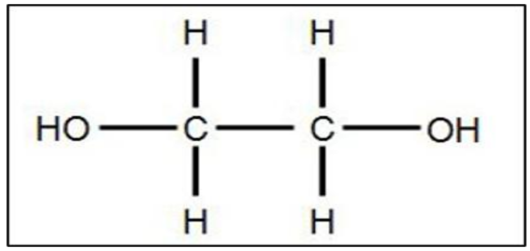

Figure No.8: Structure of Ethylene glycol

- Tetracycline: Tetracycline ($C_{22}H_{24}N_2O_8$) is a main ingredient used in this preparation. It is a broad-spectrum antibiotic that trats various bacterial infections. It works by halting bacterial growth and preventing essential protein synthesis. It can be used for treating a bacterial infection as in form of quantum dots. Tetracycline can be collected or issued from department of Pharmaceutical-Chemistry of Rashtriya College of pharmacy, Chht. Sambhajinagar.

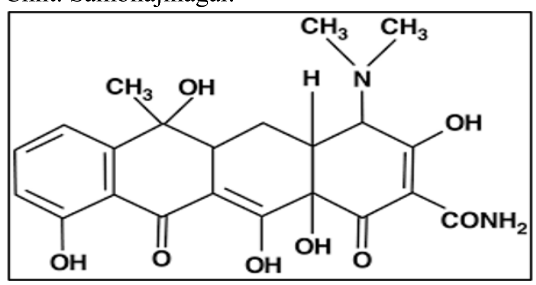

Figure No.9: Structural of Tetracycline

Instruments

- Hot air oven: A hot air oven is a fundamental laboratory and industrial tool that utilizes dry heat to sterilize equipment, dry samples, and perform thermal testing. By circulating heated air uniformly - typically between 160·C to 250·C. It eliminates microorganisms by oxidizing their cellular components. It can be used for heating the mixture of QD.

- Centrifuge Machine: A centrifuge machine is a laboratory device that uses centrifugal force to rapidly spin liquid samples, separating their components based on density. It can be used with QDs that serve two main purposes: purification/size-sorting during synthesis and particle-size analysis.

Figure No.10: Hot air oven and Centrifuge machine

Preparation of CQDs

Grind the purchased chenpi into powder. 0.1g of the powder was dissolved in 10 mL of ethylene glycol, also add 0.5g of Tetracycline and the mixture was heated in a hot air oven for 2min at 100·C. The solution turns yellowish brown, indicating the formulation of CQDs. After cooling to room temperature, the liquid supernatant was taken and centrifuged at 10,000 r/min for 10 min., while it was later filtered through a 0.22 um filter membrane to obtain the further proceeded solution. The prepared CQDs solution was stored at 4.C away from light. [30]

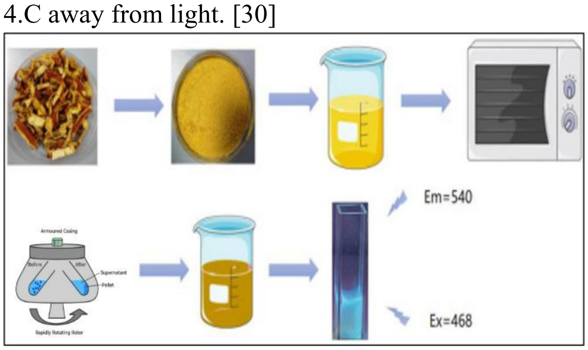

Figure No.11: Schematic illustration for preparation of CQDs.

Evaluation Test

1. Solubility Test

Solubility Testing is essential to evaluate the dispersion behavior, stability, and suitability of tetracycline-conjugated quantum dots (TC-QDs) for biomedical applications such as imaging and antibacterial therapy. It helps to determine whether TC-QDs are water-soluble or organic-solvent soluble. It can assess colloidal stability in biological media. Also, it can ensure compatibility with physiological environments. Solubility and bioavailability are key components in ensuring the drug molecule has good therapeutic action at the target site. [31]

Sample Preparation- Take a known amount of TC-QDs about 5-10 mg. also take Distilled water PBS buffer, Ethanol/ Methanol, Chloroform.

Procedure

1. Take a known amount of TC-QDs (5-10 mg).
2. Add equal amounts (5-10 ml) of different solvents:
   - Distilled Water
   - PBS buffer
   - Ethanol/ Methanol
   - Chloroform
3. Stir or sonicate each sample for 10-15 minutes.
4. Check for:
   - Clear Solution (soluble)
   - Turbidity (partially soluble)
   - Sedimentation (insoluble)
5. Check Stability after keeping sample undisturbed for 24 hours and observe precipitation or aggregation.

2. UV-Visible Spectroscopy

Sample Preparation- Solution of CQDs which are made to appropriate concentration and loaded into 10mm path length cuvettes.

Instrument Configuration

UV-Vis Spectroscopic measurements were performed on a Systronics UV-Vis Double Beam Spectrophotometer 2206TS, using touchscreen interface to set up parameters. A narrow wavelength range was chosen to better identify the first excitonic absorption peak.

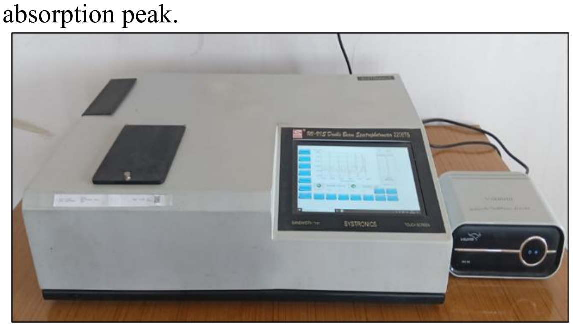

Figure No.12: Systronics UV-Vis Double Beam Spectrophotometer 2206TS

Procedure

1. A baseline measurement was taken using an empty sample chamber.
2. A cuvette containing the CQDs solution was inserted in the sample beam position, and the ethylene glycol reference cuvette was assed to the reference beam position.
3. A scan was run using the outlined parameters.

4. The first excitonic absorption peak was located by identifying the longest wavelength local maximum in the absorption spectrum.
5. That wavelength was used to calculate the diameter of CQDs in the sample.

3. Fourier Transform Infrared (FTIR) Spectroscopy

Sample Preparation- Solution of CQDs which are made to appropriate concentration and loaded

Instrument Configuration

The Cary 630 FTIR spectrometer is a flexible, benchtop FTIR instrument offering high performance and extraordinary ease-of-use in an ultra-compact design. It is a robust, reliable, and flexible benchtop FTIR instrument. Its modularity offers sampling flexibility for analysis of solids, liquids, powders and gases. Permanently aligned optics allow a wide range of modules to be swapped in and out in seconds, providing superior quantitative and qualitative information fast.

Procedure

1. Place sample in FTIR spectrometer as small as 10 microns.
2. The spectrometer directs beams of IR at the sample and measures how much of the beam and at which frequencies the sample absorbs the infrared light.
3. Identify the samples
4. Show the graph and result of CQDs

IV.RESULTS AND DISCUSSION

1. Solubility

- Highly soluble in water and PBS due to hydrophilic functional groups (-OH, -COOH, -NH_2).
- Moderately soluble in polar organic solvents (ethanol, methanol)

2. Appearance

The appearance of TC-QDs can be described based on visual observation under normal and UV light conditions.

A. Physical Appearance (Daylight)
- Form: Clear liquid or colloidal suspension
- Color: Pale yellow to light brown
- Transparency: Transparent or slightly turbid depending on concentration
- Homogeneity: Uniform dispersion without visible particles or sediment

B. Appearance under UV Light
- It shows bright fluorescence when exposed to UV light
- It can show yellow emission color

3. UV-Vis Spectroscopy

The first excitonic absorption peak corresponds to the highest energy optical transition between the discrete electronic states in the CQDs. Using Double Beam Spectrophotometer Built-in Peaks and Troughs analysis, the peak for the prepared QDs solution was found at λ= 302.4 nm. It was determined that the Absorbance of the CQDs in the prepared solution was 1. 873.This demonstrated that UV-Vis absorption Spectroscopy, carried out on the Systronics, provides a rapid method for estimating the absorption of CQDs.

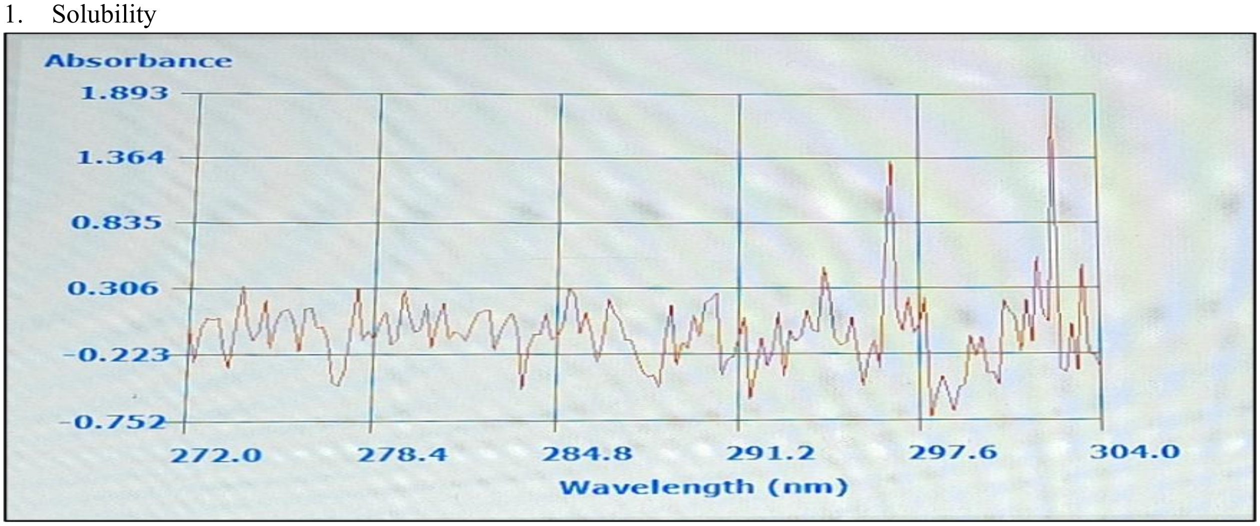

Figure No.13: UV-Vis absorption spectrum of CQDs taken from the Systronics 2206TS touchscreen interface. The peaks and Troughs function determined the first excitonic absorption peak at 302.4nm

4. Fourier Transform Infrared (FTIR) Spectroscopy

FTIR measurements were performed to investigate the functional group on the surface of the CQDs as prepared. The FTIR spectrum of CQDs show a broad O-H/N-H stretching band at ~3386.7cm^{-1}, indicating hydroxylated and nitrogen containing surface groups. The band at ~2928.4, 2879.4 and 2828.6cm^{-1} are assigned to aliphatic C-H stretching vibration. Weak bands at ~16522.0, 1616.0 and 1580.0cm^{-1}correspond to carbonyl, aromatic C=C and conjugated ring vibration. The region from ~1453.9 to 1192.1 cm^{-1} indicates C-H bending, C-N stretching and C-O stretching vibrations associated with amide/amine, phenolic and ether/alcohol groups. Strong peaks at ~1118.5 and 1059.5cm^{-1} confirm abundant C-O/C-O-C surface functionalities. The fingerprint bands between ~961.4 and 830.4 cm^{-1} are attributed to substituted aromatic C-H out-of-plane bending and ring vibrations.

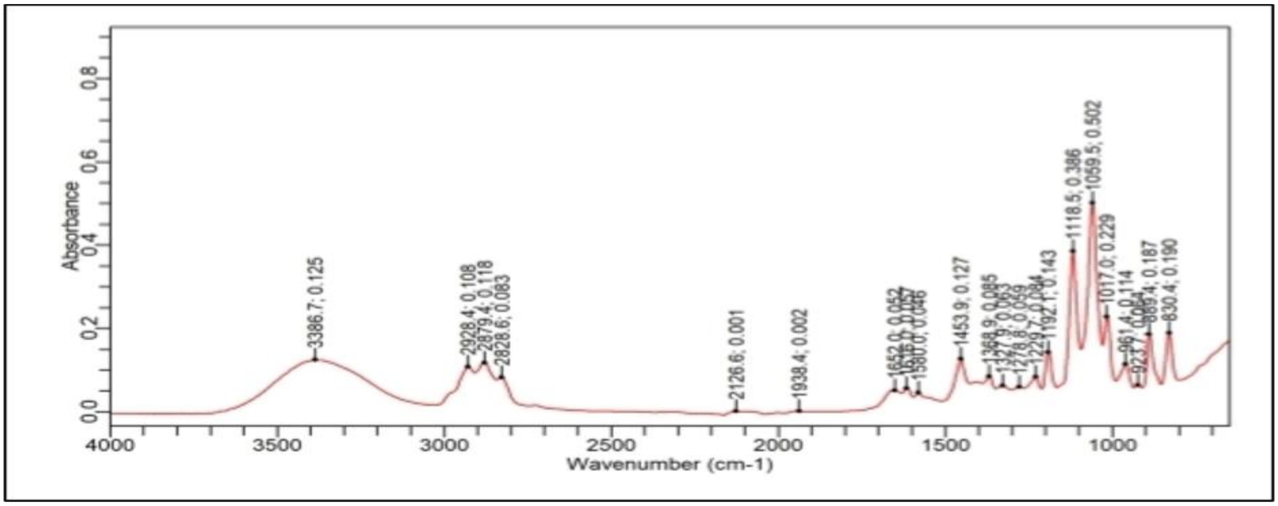

Figure No.14: Graph of the FTIR analysis of CQDs

Table No.2: FTIR
Spectral Data of Tetracycline-Conjugated QDs

Peak Number	Wavenumber (cm^{-1})	Intensity
1	830.43703	0.18963
2	889.35155	0.18666
3	923.71835	0.06448
4	961.35818	0.11438
5	1016.99967	0.22905
6	1059.54904	0.50178
7	1118.46356	0.38556
8	1192.10670	0.14326
9	1229.74653	0.08390
10	1278.84196	0.05946
11	1327.93739	0.06262
12	1368.85025	0.08539
13	1453.94900	0.12737
14	1579.96061	0.04589
15	1615.96392	0.05706
16	1651.96724	0.05198
17	1938.35725	0.00167
18	2126.55640	0.00148
19	2828.62106	0.08309
20	2879.35300	0.11768
21	2928.44843	0.10812
22	3386.67245	0.12481

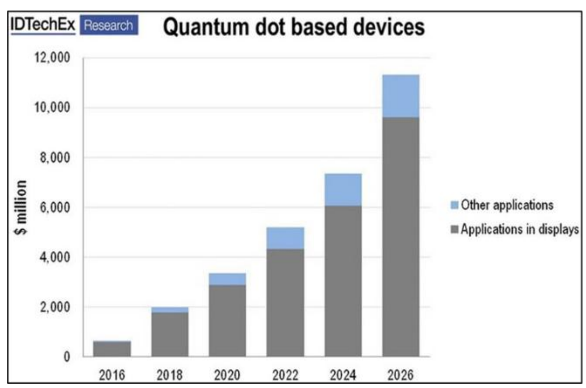

Figure No.15: QDs devices and components ($ million) 2016-2026

Future Perspective

1. Development of eco-friendly QDs (InP, ZnSe, perovskite, carbon QDs).
2. Advanced Biomedical Application
3. Next-Generation display Technologies
4. AI and Machine Learning in QD synthesis

5. Personalized medicine
6. Renewable energy and solar cells
7. Environmental and chemical sensing
8. Quantum computing and electronics
9. Green and Sustainable Nanotechnology
10. Industrial and Commercial Expansion

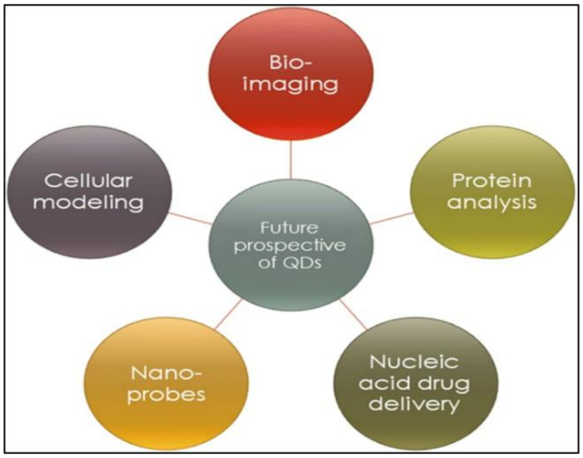

Figure No.17: Future Prospective of QDs

V.CONCLUSION

Future QD material applications exceed any expectation limits that refer to their advanced photophysical and chemical properties. The quantization size effect considers the key to variation of the QD properties due to which QDs are suitable for different types of recent application. QD materials are applicable in the future, especially in QD solar cells, biosensors, bioimaging, quantum computers, Li-Fi, photodetectors, and photocatalysis, biological uses. QDs have promising future applications due to their unique photophysical and chemical properties. Tetracycline-conjugated QDs show good aqueous solubility, which is essential for effective bioimaging and antibacterial activity. The synthesized QDs appeared as clear pale-yellow solutions and exhibited strong fluorescence under UV light, confirming successful formation. UV-Vis spectroscopy was effectively used to estimated QD size, while FTIR analysis confirmed the presence of functional groups responsible for stability and surface modification.

Conflict of interest: There is no conflict of interest.

Contribution: This project contributes to the development of multifunctional nanomaterials by synthesizing tetracycline-conjugated quantum dots that combine fluorescence imaging with antibacterial activity. The study demonstrates a simple and effective approach for targeted bioimaging and improved antimicrobial therapy. It shows improved drug efficiency and enables real-time tracking, making it useful in advanced biomedical applications.

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