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Synthesis, Optical Characterization and Bio-Compatibility Studies of GelatinBased Pure and Doped Quantum Dots

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*Abstract:***Pure and doped carbon quantum dots have been synthesized from gelatin using hydrothermal method. The synthesized CQDs and doped CQDs were characterized using UV-Vis absorption, PL-life time, Fluorescent excitation studies. The samples showed excellent fluorescent properties. The samples were tested for bio compatibility using anti-bacterial activity test, and the preliminary analysis suggest that the pure CQDs are low toxic. The pure and doped samples were proved to be good agents for bio imaging and fluorescent writing applications due to their good and stable emission life time.**

*Index Terms:***Anti-bacterial studies, Carbon quantum dots, Doping, Fluorescent emission, PL-Life time.**

I. INTRODUCTION

Quantum dots are a relatively recent discovery, with their origin dating back to the 1980s. The concept of quantum dots was first introduced by Alexei Ekimov and Louis Brus in the early 1980s, who discovered the first colloidal semiconductor nanocrystals, which they called “quantum dots”. (Leica, 2023)These dots were found to emit light at specific wavelengths, depending on their size, and were also highly photostable (Nexdot, 2016).

In the years that followed, the research on quantum dots continued to expand, with new materials and fabrication techniques being developed. Quantum dots were found to have unique properties that made them useful for a wide range of applications, including biomedicine, electronics, energy conversion, environmental remediation, optoelectronics, quantum computing, and security(Rehan M. El-Shabasy, 2021)(Lee & Lo, 2019). Today, quantum dots continue to be an active area of research, with new materials, fabrication techniques, and applications being developed. Quantum dots are expected to play an increasingly important role in the future of technology and science(Shi, et al., 2019).

Quantum dots are tiny semiconductor particles that are typically less than 10 nanometers in size. They are sometimes referred to as artificial atoms because they exhibit some of the same properties as atoms. When excited by light or electricity, quantum dots emit light with a very specific wavelength, depending on their size and composition. This property makes them useful in a variety of applications, including biological imaging, electronics, and solar cells(Ming, et al., 2012). Quantum dots are a type of nanoparticle that exhibit unique optical and electronic properties due to their small size. Unlike bulk materials, which have continuous energy bands, quantum dots have discrete energy levels, similar to atoms. This leads to a number of interesting effects, such as quantum confinement and the quantum dot size effect, which can be exploited for various applications (Sharma & Das, 2019) (Zhang, et al., 2017).

The electronic properties of quantum dots are determined by their size, shape, and composition. In general, smaller quantum dots have higher energy levels and emit light with shorter wavelengths, while larger quantum dots have lower energy levels and emit light with longer wavelengths. The emission spectrum of a quantum dot can be tuned by varying its size or composition, making them useful in a wide range of applications (Al-Douri, 2022), (Valizadeh A, 2012) (Bera D, 2010).

One of the most important applications of quantum dots is in biological imaging. Quantum dots are ideal fluorescent labels for biological molecules, cells, and tissues because they emit bright and stable light. They are also resistant to photobleaching, which is a common problem with organic dyes. In addition, quantum dots can be functionalized with various biomolecules, such as antibodies or peptides, to target specific cells or tissues (Avantama, 2020)(Nasrollahzadeh, 2019). They are also used in electronics, color display lights, solar cells etc (Pavel Zrazhevskiy, 2010).

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Carbon quantum dots (CQDs) are a type of quantum dot that are composed primarily of carbon atoms. They are typically smaller than 10 nanometers in size and exhibit unique optical and electronic properties due to their size and composition. CQDs have recently emerged as a promising material for various applications, including biomedical imaging, sensing, and energy conversion (Prathumsuwan, 2018).

Despite their promising properties and potential applications, there are still several challenges that need to be addressed in the field of CQDs. One of the main challenges is the synthesis of CQDs with high purity and reproducibility. The synthesis process can be complex and requires careful control over the reaction conditions to ensure that the resulting CQDs have the desired properties. CQDs can be synthesized from a variety of carbon sources, including carbon nanotubes, graphene, and organic molecules such as glucose and citric acid. The synthesis process typically involves the use of high temperatures and/or chemical reagents to break down the carbon source into small particles, which are then functionalized with organic molecules to improve their stability and solubility in water or other solvents. The present study describes the synthesis of pure and doped carbon quantum dots from gelatin using hydrothermal bottom-up method. It also details the fluorescent study of synthesized quantum dots and the biocompatibility study. (Heath McCabe, 2019).

In conclusion, carbon quantum dots are a promising class of nanomaterials with unique optical and electronic properties. They have potential applications in biomedicine, energy conversion, and electronics, among other fields. However, there are still several challenges that need to be addressed in the field of CQDs, including the synthesis and characterization of CQDs with high purity and reproducibility (Xie, et al., 2018). The present study is an attempt to synthesize carbon quantum dots from gelatin using hydrothermal bottom-up method and to modify the properties by doping with succinic acid (SA-CQD) and cobalt (Co-CQD) as dopants. It also studies the fluorescent analysis, PL life time, Spectrophotometric analysis and bio compatibility studies.

II. EXPERIMENTAL

A. Materials used for synthesis

Gelatine, Succinic acid, Cobalt, de ionized water

B. Equipment

We use a Teflon autoclave(A. Oyawale, 2007)(P. Hubert, 2012)and muffle furnace made by Indfurr Superheat furnaces, Chennai, for the synthesis of carbon quantum dots. The autoclave is designed to withstand high temperature up to 220°C and to maintain high pressure. So, the required temperature of 180°C for the synthesis can be achieved using this. It can also used for synthesis at higher temperatures, for varying the fluorescent properties of CQD. The muffle furnace is a furnace that can maintain high temperature for hours as per the set program.

Figure 1: Hydrothermal Autoclave

Figure 2: Muffle Furnace

C. Synthesis of Pure Carbon Quantum Dots

The hydrothermal(Aimable, 2021) bottom-up method using gelatine as a precursor offers a cost-effective and relatively straightforward approach for producing CQDs. In the hydrothermal synthesis of CQDs from gelatine, the bottom-up approach is employed to create these nanoscale semiconducting particles. The process begins by accurately measuring 0.5 grams of gelatine, which is then dissolved in 25 mL of Doubly De-ionized water at room temperature while ensuring continuous stirring. This gelatine solution is then carefully poured into a 50 mL Teflon autoclave pressure vessel, designed to withstand high pressure and temperature. Subsequently, the autoclave vessel, containing the gelatine solution, is placed within a muffle furnace. The muffle furnace provides a controlled high-temperature environment necessary for the synthesis process. The temperature is set to 180°C, and the vessel is subjected to this heat for a duration of 4 hours. The combination of heat and pressure within the autoclave vessel triggers a hydrothermal reaction, enabling the transformation of gelatine into quantum dots. After the completion of the 4-hour heating period, the muffle furnace is turned off, allowing the autoclave vessel to gradually cool down to room temperature. This cooling phase is essential for stabilizing the synthesized CQDs. Once cooled, the resulting quantum dots can possess unique optoelectronic properties due to their nanoscale dimensions.

Figure 3: Pure CQD and Water under visible light

Figure 4: Pure CQD and Water under UV light

D. *Synthesis of doped Carbon Quantum Dots*

Many samples were tried as dopants and the one showed significant result among them are succinic acid and cobalt. To prepare Cobalt-doped CQDs, a one-step hydrothermal synthesis method was employed. Initially, 0.5 g of gelatine was dissolved in 25 ml of doubly de-ionized water through stirring at room temperature. To this solution, 0.02 g of Cobaltous nitrate was added and completely dissolved by continuous stirring. The resulting mixture was then poured into a 50 ml Teflon autoclave pressure vessel and subjected to a temperature of 180°C for 4 hours using a muffle furnace. The hydrothermal reaction took place under these controlled temperature and pressure conditions. After completion, the autoclave was removed from the furnace and allowed to cool. Upon cooling, the solution exhibited a slight orange tint, and when exposed to UV light, it displayed photoluminescence, indicating the presence of quantum dots.

Similarly, the synthesis of succinic acid-doped CQDs followed a similar hydrothermal process. In this case, a suitable amount of 0.025 g of succinic acid was dissolved in a gelatine solution (0.5 g per 25 ml). The solution was prepared by stirring at room temperature using a magnetic stirrer. Subsequently, the solution was transferred to a 50 ml Teflon autoclave pressure vessel and placed inside a muffle furnace. The temperature was set to 180°C, and the reaction was allowed to proceed for 4 hours. The heat and pressure within the autoclave facilitated the formation of succinic acid-doped CQDs through the hydrothermal reaction. After the heating process, the Teflon autoclave was gradually cooled to room temperature. The resulting solution, when transferred to a glass beaker, appeared darker in colour compared to the pure solution. It also exhibited photoluminescence upon irradiation with UV light, indicating the successful formation of quantum dots.

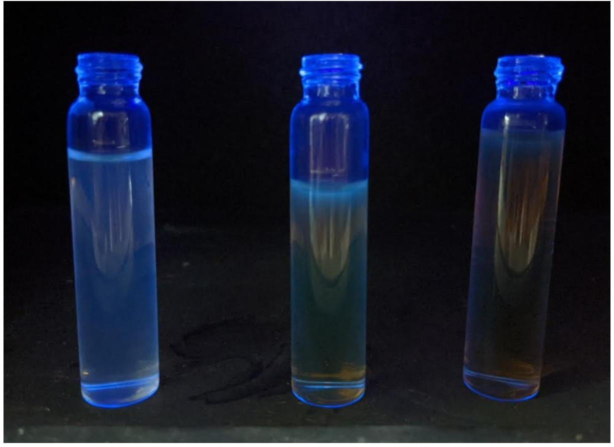

Figure 5: Pure CQD, Succinic acid doped CQD and Cobalt doped CQD under UV light

The variation in colour observed among the pure CQDs, Cobalt-doped CQDs, and succinic acid-doped CQDs can be attributed to differences in particle size, absorption properties, or the presence of distinct functional groups resulting from the doping process. These factors play a crucial role in determining the optical characteristics of the quantum dots, leading to variations in their visible light absorption and emission properties and, consequently, resulting in different shades of colour.

III. CHARACTERIZATION

A. *Photo luminescence*

It is the phenomenon of emission of light after being excited to a higher level. Fluorescence and Phosphorescence are two categories of photo luminescence. In fluorescence, the material absorbs low wavelength (high energy) radiation and emits high wavelength radiation. Photo luminescent studies of grown samples are conducted and the results obtained are shown here. The samples are excited using UV radiation of wavelength 315 nm and 341 nm (Figure 6). The pure and doped samples show emission above 400nm, which is visible light. For 315 nm, excitation, pure CQD gives an emission peak at 408.5 nm and doped samples show emission at higher wavelengths. But for excitation with 341 nm, pure CQD show emission at 448 nm, while doped samples show emission at lower wavelengths. As the excitation wavelength increases, the emission wavelength also increases in case of individual samples as shown in figures 7 to 9. But the samples show some anomalies when they are irradiated with light in the visible region and it accounts due to a photon up conversion. The emission data is shown in table 1.

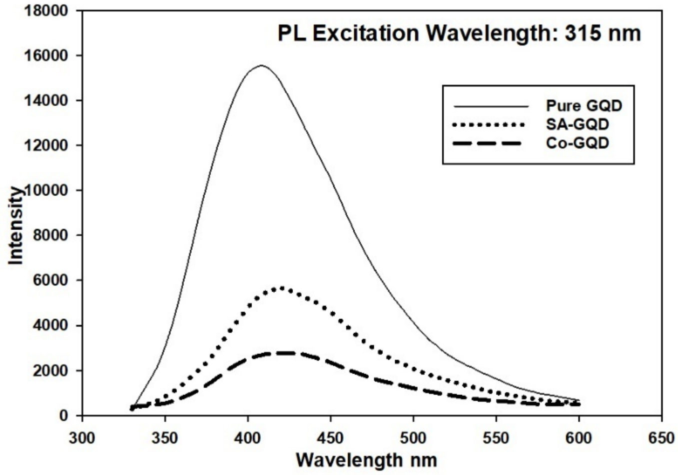

Figure 6: PL Emission of pure and doped samples at 315 nm

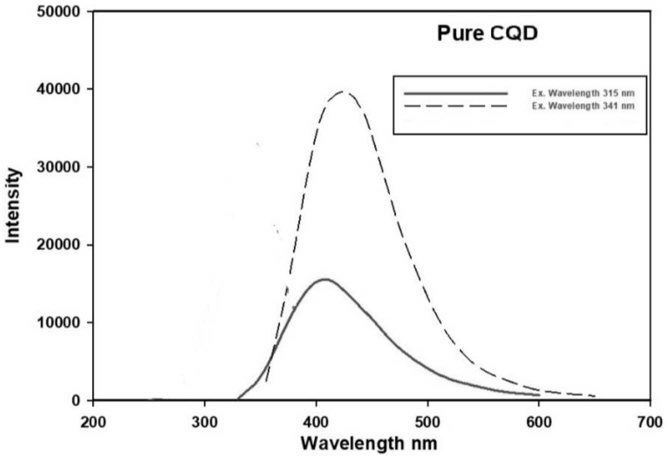

Figure 7: PL Emission of Pure CQD

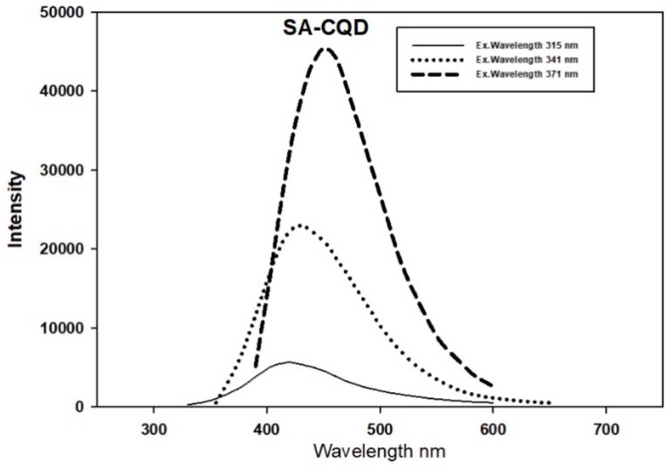

Figure 8: PL Emission of SA-CQD

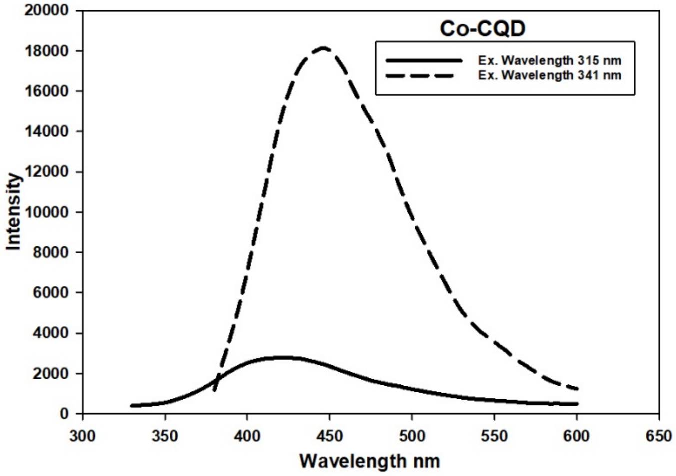

Figure 9: PL Emission of Co-CQD

Table 1: PL Emission of pure and doped CQD for various excitation wavelengths

Excitation wavelength	315nm	341nm
Pure CQD	408.5nm	448nm
SA-CQD	419.63nm	432.5nm
Co-CQD	422.5nm	444.1nm

B. Photon Up-Conversion

It is the process of absorbing low energy visible light and to emit high energy ultra violet light. In this process, sequential absorption of two or more photons of higher wavelength (low energy) happens and that leads to emission of low wavelength (high energy). The grown pure and doped CQDs were irradiated with visible wavelength 420 nm and the emission spectrum is studied and is shown in figure 10. The emission spectrum belongs to ultra violet region, which is a clear evidence of photon up-conversion. The emission details are given in table 2. For an excitation wavelength of 420 nm, the samples show emission 340nm, 371.2 nm and 364.8 nm respectively.

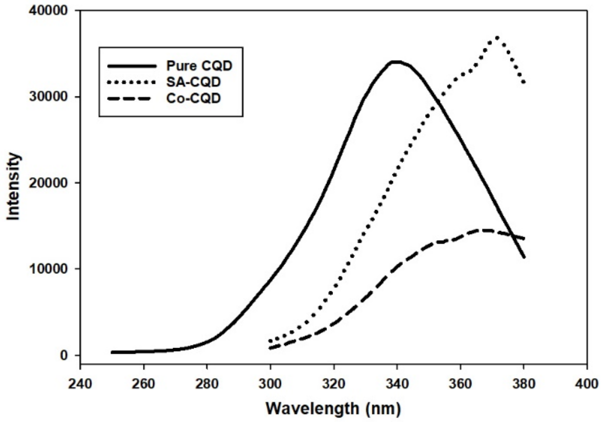

Figure 10: Photon up-conversion

Table 2: Photon Up-Conversion Emissions

Excitation wavelength	420 nm	
Pure CQD	340 nm	Emission Wavelength
SA-CQD	371.2 nm	
Co-CQD	364.8 nm	

C. PL-Life Time

PL Life time or fluorescence life time is the time that the material spends in the excited state after irradiated with a photon and before emitting a photon and returning to the ground state. PL life time is an intrinsic property of the sample. It does not depend on the thickness, concentration, intensity of radiation etc. The Photo luminescent life time study of the samples were done and are shown in figure 11. The pure and doped samples show not much difference in PL life time. The high resolved image in figure 12 shows that the slight variation in PL life time of three samples.

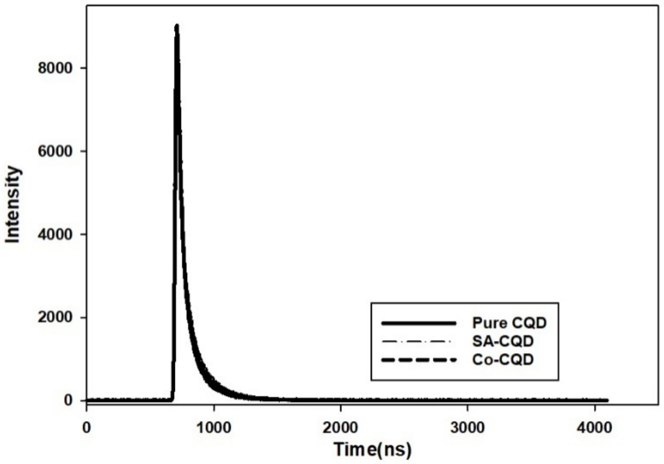

Figure 11: PL Life Time

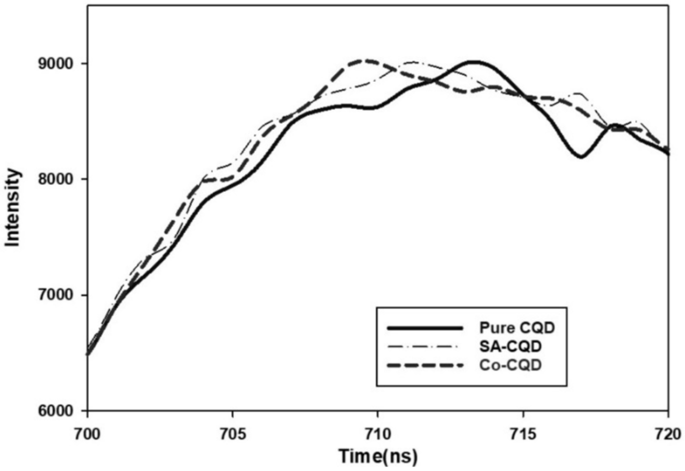

Figure 12: PL-Life time (Enlarged)

D. Absorbance Studies

UV-Vis absorption studies are used to characterize the optical absorption properties and the nature and quality of the of the samples. Optical properties can be analyzed from the transmittance or absorbance spectra obtained from UV-Vis-NIR Spectroscopy. The UV-Vis analysis of the CQDs were done in the wavelength range of 200 nm to 800 nm. The spectra shows that absorption range varies by doping with samples like succinic acid or cobalt. The absorption spectra is shown in the figure 13.

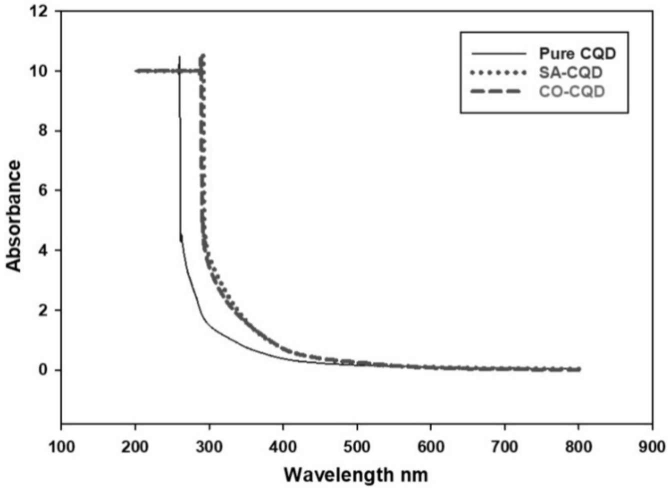

Figure 13: Absorbance Spectra

E. Band Gap Analysis

Optical bandgap is an important parameter to know for applications of CQDs. Various types of interactions of the material with radiations, like transmission, reflection, emission, refraction, scattering and diffraction, determines the optical properties. All these directly or indirectly depends on the optical bandgap of the material. Optical bandgap can be determined from the absorption data by plotting the Tauc plot and drawing tangent to the X axis where energy of photon is plotted. Figure 14 shows the Tauc Plot and table 3 shows the band gap obtained for the three samples. It is noticed that the doped CQDs show lesser value of bandgap in comparison to the pure samples. This clearly indicates that the band gap can be modified by doping with suitable samples to make it convenient for various applications.

Table 3: Band Gap Analysis

Pure CQD	4.62 eV
SA-CQD	4.2 eV
Co-CQD	4.32 eV

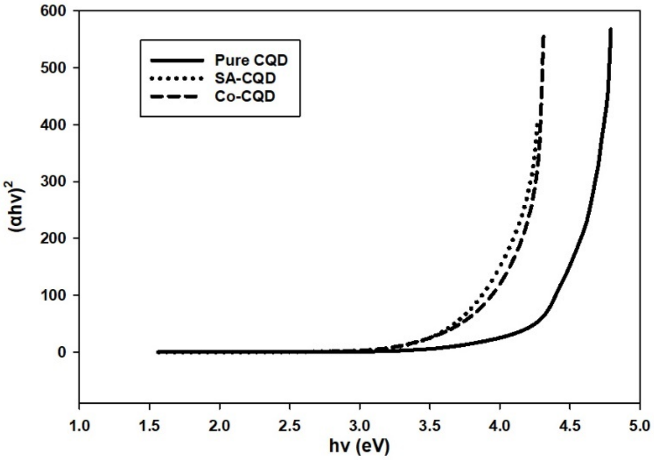

Figure 14: Tauc Plot

F. Bio compatibility studies

Along with the other characterization techniques employed, the grown samples were also tested for its biocompatibility, to ensure the safety of the samples for particular uses in relation to living organisms and their biosensing applications. This is to ensure that the grown samples do not induce any unwanted threat to life or any type of infection. While in contact with living organisms.

Pseudomonas and Staphylococcus types of bacteria swabs were used in this test. Bacteria swabs were taken from the bacteria culture and transferred to molten sterilized molten agar in a dish. Then 10 µL of three different CQD’s are spotted on to this solutionand kept in to the incubator at 37°C for 24 hours. After 24 hours it is noticed that the bacteria growth is equal in all areas of the solution. This shows that the CQD samples are not affecting life of the two bacteria used for the study. So, this can be considered as a preliminary analysis for its biocompatibility and further in-depth studies in this regard are needed before actual application.

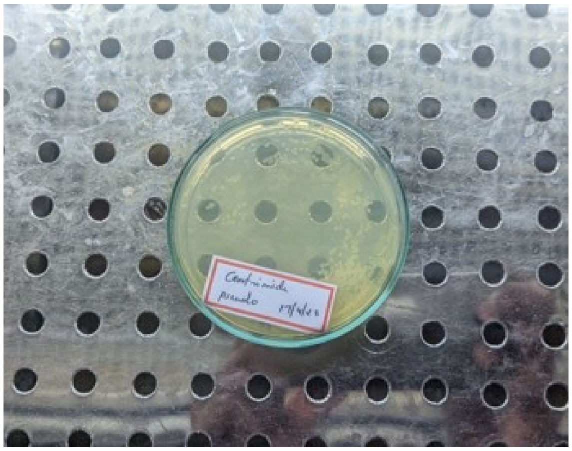

Figure 15: Pseudomonas Bacteria in Protein Solution

Figure 16: Pseudomonas Bacteria in Protein Solution with Pure and Doped CQD spots

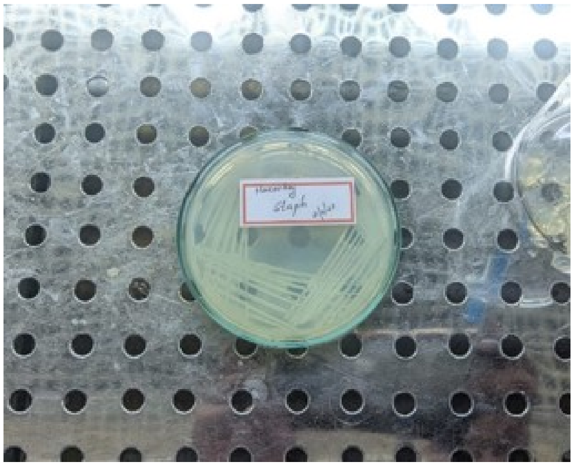

Figure 17: Staphylococcus Bacteria in Protein Solution

Figure 18: Staphylococcus Bacteria in Protein Solution with Pure and Doped CQD Spots

IV. RESULT AND DISCUSSION

Good quality carbon quantum dopes were synthesized from gelatin. Their optical properties were investigated. The U-V exposure shows the high fluorescent action of the grown samples. The detailed photoluminescent studies showed the fluorescent emission wavelengths for the samples at various excitation wavelengths. The excitation at 315nm gave an emission wavelength of 408.5nm for pure CQD while the doped samples show lesser emission wavelength of 419.63nm and 422.5nm for SA-CQD and Co-CQD respectively. But for excitation wavelength of 341nm, the pure sample showed emission of 448nm while the doped samples showed 432.5nm and 444.1nm for SA-CQD and Co-CQD respectively.

It is also noticed that the pure CQD and doped CQD's showed a photon up conversion when excited with visible light of wavelength 420 nm. In this phenomenon the CQD absorb low energy (Visible Light) photon and emit higher energy photon (Ultra Violet). This is an area of future research to find potential applications and modification in material properties.

The UV-Vis absorption studies of the grown samples were carried out and the pure and doped samples showed absorption in the UV region as expected. The band gap of the samples was determined using Tauc plot and are modified on doping. In the case of both the doped CQD's, the bandgap is seen to be decrease from the 4.62 eV to 4.2 eV and 4.32 eV for SA-CQD and Co-CQD respectively.

Preliminary biocompatibility studies were also carried out using staphylococcus and Pseudomonas bacteria. The studies indicate that the synthesized pure and doped CQD's are not opposing the existence of life in it. This is also a positive result as the application of CQDs include bio sensors.

V. CONCLUSION

Pure and doped carbon quantum dots were synthesized from gelatin using hydrothermal bottom-up method. They were characterized for their photo luminescent character, PL-Life time, UV-Vis absorption, Band Gap and biocompatibility. It is noticed that the optical properties of CQD showed significant modification with doping.The pure and doped quantum dots developed are supporting life in them. The optical band gap of doped samples show reduction compare to pure CQD. So, by suitably doping we can modify the properties for various application. A photon up-conversion result is obtained during the photo luminescent studies, which a good scope for future studies.

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