Photon up-conversion in pure and doped carbon quantum dots synthesized from gelatine

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ABSTRACT

Photon up-conversion is the process of absorbing lower-frequency radiation and emitting higher-frequency radiation, in contrast to the case of fluorescence. Pure and doped carbon quantum dots (CQD) have been synthesized from gelatin using the hydrothermal method. The synthesized CQDs and doped CQDs were characterized using UV-Vis absorption, PL-life time, and fluorescent excitation studies Along with the fluorescent nature the pure and doped samples showed photon up-conversion and are being investigated. It is the process of absorbing low-energy visible light and emitting high-energy ultraviolet light. The pure and 2 doped samples show up-conversion. Further investigations were done to study the variation in up-conversion frequency with variation in excitation frequency. The up-conversion frequencies vary with dopants but showed a stable emission for various excitations. Biocompatibility studies of the grown samples also conducted to check the activity of the samples and the up-conversion UV light on the biological specimens.

Keywords: Photon up conversion, Carbon quantum dots, fluorescent emission, Doping, PL-Life time, bottom-up method, Gelatin based quantum dots, Absorbance.

1. INTRODUCTION

In a relatively recent discovery in early 1980's, the concept of quantum dots was first introduced by Alexei Ekimov and Louis Brus. These dots were found to emit light at specific wavelengths, depending on their size, and were also highly photostable. From there, the developments and application in the field of quantum dots was very fast. They have unique properties that made them to use in applications like biomedicine, electronics, energy conversion, environmental remediation, optoelectronics, quantum computing, and security. Quantum dots is an active area of research, with new materials, fabrication techniques, and applications being developed. They are expected to play vital role in the future of technology and science. The size, shape, and composition determine the electronic properties of quantum dots. The emission spectrum of a quantum dot depends on its size or composition, making them useful in a wide range of applications. Smaller quantum dots have higher energy levels and emit light with shorter wavelengths, while larger quantum dots emit light with longer wavelengths. Their wide variety of applications were reported in many journals.

Photon up-conversion or photon assisted up-conversion photoluminescence is the phenomenon of boosting energy of an emission photon to be more than that of the excitation photon. This occurs because of the phonon- electron coupled electronic states, which is the same mechanism that works for the conventional down conversion photo luminescence. The study showcases that pure and doped quantum dots show good yield of photon up conversion along with the conventional down conversion photo luminescence. Here visible-ultra violet up conversion carbon quantum dots are prepared from gelatine using hydrothermal bottom-up method. The photo luminescence spectra proved that the pure and doped CQDs convert 420 nm and 520 nm visible light in to ultra violet light along with the normal fluorescence down conversion from ultra violet to visible light. Pure and doped carbon quantum dots (CQD) have been synthesized from gelatin using the hydrothermal method (Figure 1). The synthesized CQDs and doped CQDs were characterized using UV-Vis absorption, PL-life time, and fluorescent excitation studies Along with the fluorescent nature the pure and doped samples showed photon up-conversion and are being investigated. It is the process of absorbing low-energy visible light and emitting high-energy ultraviolet light (Figure 2). The pure and 2 doped samples show up-conversion. Further investigations were done to study the variation in up-conversion frequency with variation in excitation frequency. The up-conversion frequencies vary with dopants and their excitation frequency.

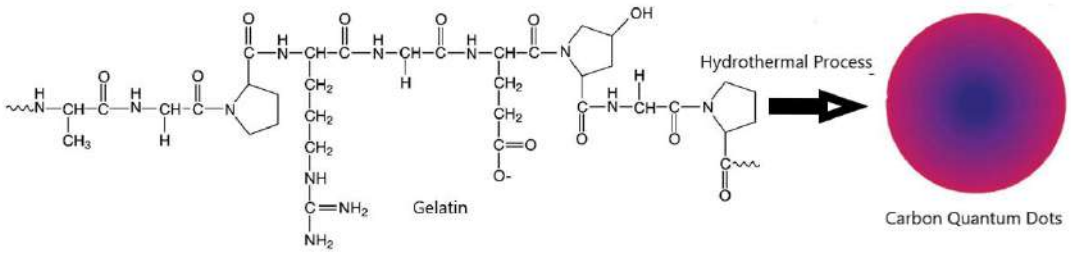


Figure 1: Carbon Quantum Dots from Gelatine

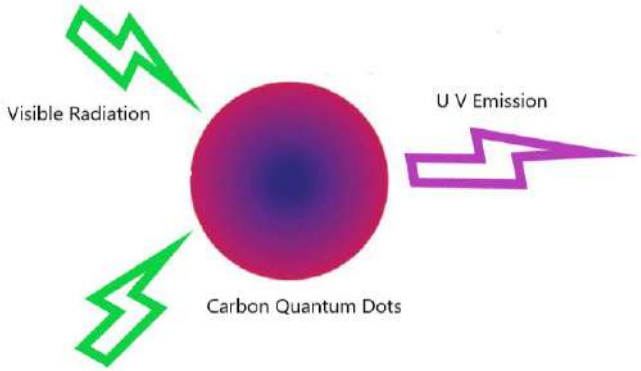


Figure 2: Photon up-conversion

2. EXPERIMENTAL

2.1 Materials used for synthesis

Gelatine, Succinic acid, Cobalt, de ionized water

2.2 Equipment

We use a Teflon autoclave and muffle furnace for the synthesis of carbon quantum dots. The required temperature of 180^{o}C for the synthesis can be achieved using the autoclave. The same autoclave can be used to synthesis CQDs at higher temperature for varying the fluorescent properties.

2.3 Synthesis of pure carbon quantum dots

The hydrothermal bottom-up method is used to synthesise CQDs.0.5 g of gelatine in dissolved in 25 ml doubly de-ionized water at room temperature and continuously stirred well using magnetic stirrer. Then the solution is poured in to a Teflon autoclave and placed inside a muffle furnace to heat it at 180 0C for 4 hours. Due to the high pressure and temperature inside the autoclave, hydrothermal reaction occurs, that transforms gelatine in to CQD. After 4 hours of heating, the autoclave is allowed to cool slowly to acquire unique optoelectronic properties due to their nanoscale dimensions.

Out of many samples tried, succinic acid and cobalt showed significant variations in optical properties. For the synthesis of doped CQD also, the hydrothermal bottom-up synthesis is used. While adding 0.5g of gelatine to 25 ml of doubly de-ionized water, 0.02g of dopants were added along with continuous stirring. The resultant solution is then transferred to Teflon autoclave and then kept in the muffle furnace for 4 hours at 180 ^{o}C and then cooled slowly. The resulting solution was darker in colour in visible light than the pure CQD. The doped samples also showed fluorescence upon irradiation with U V light, showing the successful formation of CQDs. The colour variation (Figure 3) 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.

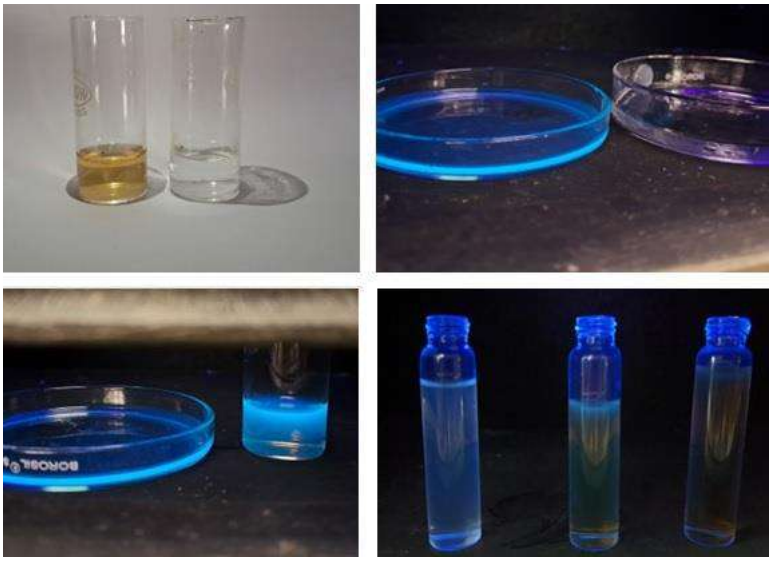


Figure 3: Carbon Quantum Dots (i) CQD and pure water irradiated with visible light (ii) CQD and pure water irradiated with U V light (iii) CQD under UV irradiation (iv) Pure, SA-CQD and Co-CQD under UV irradiation

3. CHARACTERIZATION

3.1 Photo luminescence

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(Figure 4). 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. The PL-Life time of the samples are also shown in Figure 4.

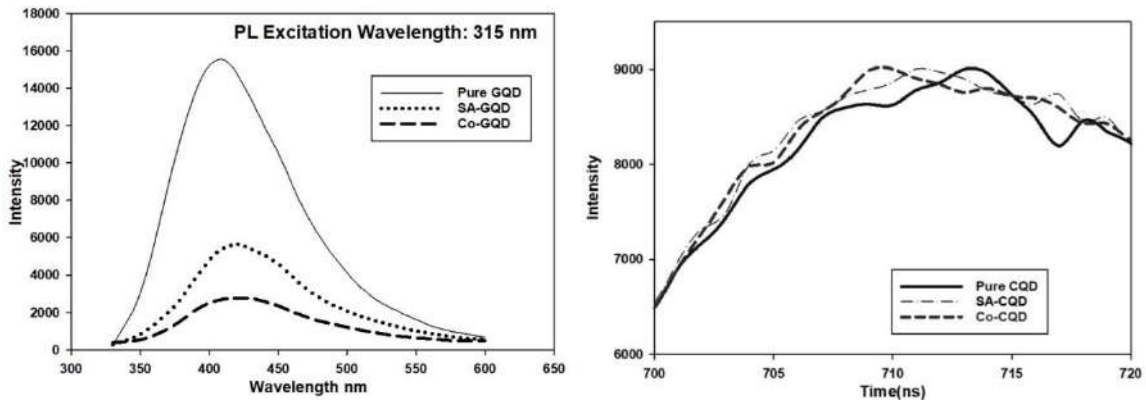


Figure 4: (i) Photo-luminescent Excitation (ii) PL-Life time Study

3.2 Photon up conversion

Even though belongs to photoluminescence, photon up-conversion is opposite to fluorescence, where low energy photons are emitted. 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 460 nm and the emission spectrum is studied and is shown in figure 4. The emission spectrum belongs to ultra violet region, which is a clear evidence of photon up-conversion. It is noticed that the emission wavelengths are nearly the same pointing towards a stable up-conversion. The emission details are given in table 1. For an excitation wavelength of 420 nm, the samples show emission 340nm, 371.2 nm and 364.8 nm respectively.

Table 1: Photon up-conversion

Excitation wavelength	420 nm	460 nm	
Pure CQD	340 nm	350 nm	Emission Wavelength
SA-CQD	371.2 nm	348.2 nm	
Co-CQD	364.8 nm	345.5 nm	

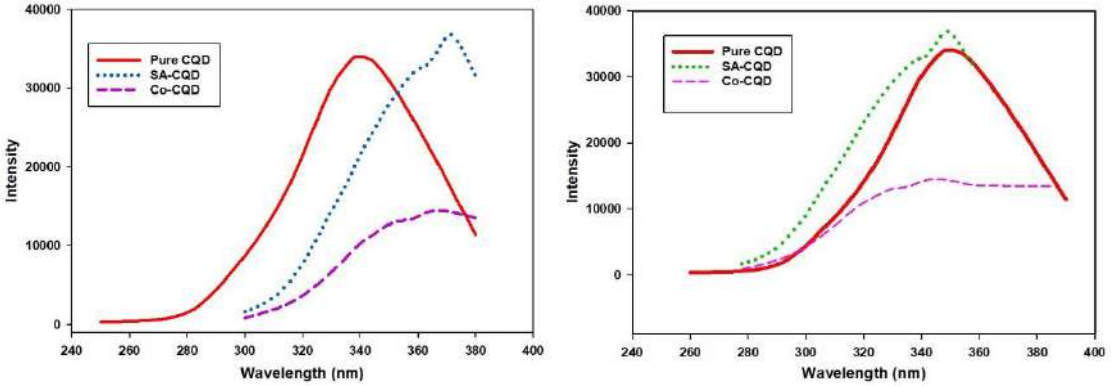


Figure 5: Photon up-conversion for excitation at (i) 420 nm (ii) 460 nm

3.3 Band Gap Energy

The band gap energy of pure and doped CQDs were determined from the Tauc plot using Absorbance data obtained. The Band gap of the samples are listed in table 2.

Table 2: Bandgap of pure and doped CQD

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

3.4 Biocompatibility studies

The bio compatibility of the grown samples was tested for two reasons. One is to ensure that the grown samples are not poisonous that adversely affect life and the other thing is to check the emitting UV influence on life. Pseudomonas and Staphylococcus types of bacteria swabs were used in this test (Figure 6). But it is noticed that after a day's duration, the bacteria growth was not affected when it is kept in dark. It shows not much adverse effect when it is kept in mild sunlight also, showing that the up-conversion emission of U.V light is of low intensity and not harmful for life. But this test has to be extended to high intense visible excitation.



Figure 6: Bio compatibility studies(i) Pseudomonas (ii) Staphylococcus

4. RESULTS AND DISCUSSION

Gelatine based pure and doped CQDs are synthesized using hydrothermal method. Their photoluminescent and up-conversion properties were investigated. Various excitation frequencies used to study the photoluminescence. The excitation at 315nm gave an emission wavelength of 408.5nm, 419.63nm and 422.5nm for pure CQD, SA-CQD and Co-CQD respectively. For excitation wavelength of 341nm, the emission wavelengths are 448nm , 432.5nm and 444.1nm for pure CQD, SA-CQD and Co-CQD respectively. Photon up-conversion is investigated with excitation wavelengths of 420 nm and 460 nm . The emission frequencies are determined and it is noted that the emission frequencies for both the excitations are nearly same. This shows that for wide range of excitation energy in the visible spectrum, the emission is stable near 340 nm to 370 nm.

5. CONCLUSION

Pure and doped carbon quantum dots were synthesized from gelatin using hydrothermal bottom-up method. Their photoluminescent character is studied. The photon up conversion frequency variations due to various excitation energies also noticed. It is also noticed that the up-conversion frequency varies with variations in dopants.

6. FUTURE POSSIBILITIES

A detailed investigation can be conducted to know the variations in photon up-conversion due to different factors like concentration of the dopant, temperature of formation of CQDs etc. The up-conversion can be effectively used to support, photocatalytic reactions. So, this can be used as a biosensor that activates in the presence of visible light. Also, this can be used to destroy germs from a sample by keeping it at sunlight, by producing U V radiations that destroys the germs.

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