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Optical and Structural Properties of Carbon Dots Synthesized From 3 Juices (Lemon, Onion and Papaya) by Green Synthesis Method

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ABSTRACT

CQD are required tool for traceable targeted delivery, biomedical research, and different therapy applications. In this work, we use lemon, papaya and onion which is commonly found in street markets are used for synthesis of carbon dots. Structural and optical properties of synthesized dots were characterized using XRD, Raman, UV – Vis and FTIR spectroscopic methods. Carbon dots suspended in DI water exposed to Mid UV (255 nm – 312 nm) emits fluorescent light of green color confirmed the formation of CDs. UV-Vis characterization showed and absorption prominent peak between 220 to 375 nm. The energy gap of CDs is found to be 3.241 eV. Its refractive index is estimated to be 2.0745. Showing that these CDs are potential candidate for detector applications. XRD spectra depicts that the absorption heap between 2θ values 15 to 25 indicate the formation of nanoparticles. It gives an additional information that the powder contains crystalline structure (peaks at 2θ values = 24.2, 28.34, 29.8, 30.84, 31.32, 34.08, 40.5, 43.22, 50.16, 58.58, 66.36, 73.66). Raman characterizations indicated the presence of prime functional groups. It is observed that the peaks in the region 1000 – 1250 cm^{-1} having functional group υ(C=S) and is Raman strong and IR weak. The peak region around 1400-1470 cm^{-1} δ(CH2) δ(CH3) is in Raman medium and in IR medium. FTIR Characterization the sample is Indicated as two regions finger print and Group and identifying functional Group. In this paper, we explain the current progress of CQD in the biomedical field, focusing on their synthetic methods and characterization with critical insights into facilitating their potential in various applications.

Keywords: Carbon Dots, CQD, Green Synthesis Method, Lemon, Onion, Papaya

INTRODUCTION

The Russian physicist Alexey Ekimov in 1984 was the first to discover the quantum dots (QDs) in glass crystals [9,17,18]. Carbon dots (CDs) are a class of fluorescence nano materials, whose diameter is less than 10nm, that can also exhibit same behavior as quantum dot. Literature shows different synthesis and characterization methods for CDs, which are less harm compared to certain heavy metal based quantum dots & it also useful in nature in the field of sensors, device and biomedical applications.

Earlier, synthesis of CDs was done by using top-down method, whereby graphite was obtained through multiple steps using chemicals to transform it into more usable graphite oxide, before break it down to nano size. Another method is by bottom-up synthesis method where smaller molecules are combine & convert to form CDs, which are increasingly attractive due to their implementation QDs.[13]

Recently, they have synthesized using renewable Raw materials. CDs could be

divided into graphene quantum dots (GQDs), carbon nano-dots (CNDs), and polymer dots (PDs) before 2015 [15,16]. Also classified the CDs into GQDs, CNDs, and carbon quantum dots (CQDs). They are much diverse in the application development in areas such as sensing, bio-imaging, anti-bacterials, fluorescent, patterning inks, photo catalysis etc. [3,13]

Herein, we recap all kinds of synthesis methods for the preparation of CDs, especially focused on the CPDs and relevant synthesis methods (hydrothermal, solvothermal, microwave-assisted method, etc.).[3,19,20,21,22] In literature, the structure and properties of CPDs are discussed in detail, the effects of synthesis conditions on the structure and properties are analyzed [1]. Though different CDs possess different properties and applications, there is need of development of comprehensive model constituting the size, structure and property oriented applications. New interpretations of results may lead to the development of advanced applications. Yield, cost and simple synthesis process may also finds applications at common levels. In this view we have synthesized CDs by green synthesis technique. Their properties have been studied using various techniques are reported in this paper.

In this work we use lemon, papaya and onion for the synthesis of carbon dots. Synthesized CD's are studied for structural and optical properties using XRD, Raman, UV – Vis and FTIR spectroscopic methods.

EXPERIMENTAL

CHEMICALS AND MATERIALS

All chemicals were of analytical grade and freshly distilled and deionized water (TDS = 0, pH = 5.5 - 7) was used to prepare all solutions.

For the synthesis of fluorescent CDs, onion, lemon and papaya were purchased from the local market in Chintamani, India and DI water was used for preparation for samples[26,27]. 100ml of 1N ammonium hydroxide solution was prepared by using 25% purity of ammonium of concentration 13.3N, 1N of ammonium hydroxide solution [1N NH_4OH = 92.5 ml of DI water + 7.5ml of 25% NH_4OH]. This solution of 1N ammonium hydroxide was used for preparation of samples.[23,24,25]

Carbon dots were synthesized by rapid one step microwave-assisted carbonization method[19,20,21,22]. The liquid sample was prepared as given below.[14]

The fresh papaya, lemon and onion were peeled out the skin of both papaya and onion, lemon is squeezed to obtain juice. Then 30.0 ml of papaya, lemon and onion juice each were extracted using a steel mixer jar. 16 ml DI water was added to above solution then add 23ml freshly prepared ammonium hydroxide (NH_4OH). [26,27] The solution was transferred into 250ml Erlenmeyer flask, then it was placed in microwave oven at 1700w for 5 minutes. In order to remove the microbes present in sample we use domestic micro – wave oven. After bringing it to the room temperature, it was kept in muffle furnace at 162℃ for 2 hours, we use muffle furnace to eliminate contamination of the samples. Later, on it was centrifuged for 3 hours at 6400rpm. In order to separate the larger particles present in sample centrifugation is done. Then the solution is kept at freezer for further use. Here, purpose of freezing is, if the sample is kept outside their will be formation of yeast in order to avoid that, sample is kept in freezer.

The same procedure is carried out for preparation of powder sample but here we use 100ml each which is extracted using a steel mixer jar and kept in micro-wave oven. After bringing it to the room temperature the beaker was placed in a Hot air oven at 242℃ for 54 hours 25 minutes. Then the powder sample obtained are taken into crucibles and allowed to heat in a muffle furnace at 400℃ for 5 hours [calcination]. Then it is allowed to cooled for room temperature. Using Mortar pestle the sample was crushed into a fine powder. Later, the powder sample was ready for further characterization.[2,6,7]

Figure 1. Synthesis of CDs from Lemon, Papaya and Onion Juice.

CHARACTERIZATION OF CDs

Numerous techniques may be used in order to characterize C-dots, for example, ultraviolet (UV) spectroscopy, X-ray diffraction (XRD), Raman spectroscopy and fourier-transform infrared spectroscopy (FTIR). [3]

The absorption spectra were obtained by UV – Vis spectrophotometer using liquid sample (SHIMADZU, model UV - 2600(230V), India). XRD patterns were determined using powder samples by X-ray diffraction (X-RAY DIFFRACTOMETER – 7000 X EMERGED). Raman peaks are determined by using the powder samples by Raman spectrometer (HORIBA Scientific, Labram HR Evolution, India). FTIR spectra were recorded by FTIR spectrometer by using powder sample (spectrum 3 FT – IR spectrometer, India).

In order to remove the microbes present in sample we use domestic micro – wave oven (Samsung, 1700w, India). The solid particles produced in the synthesis was separated by centrifugation method (Micro Refrigerated Centrifuge, Microprocessor Based Centrifuge, Microcontroller cum Indication 6400 rpm). To check the presence of CDs we use UV illuminator (EQUIPTRONICS, MODEL NO : EQ 785, UV Trans illuminator with German UV filter and safety switch and indicator view size : 150 X 150).

RESULTS AND DISCUSSIONS

VARIATION OF UV – VIS SPECTRA, XRD SPECTRA, RAMAN SPECTRA AND FTIR SPECTRA FOR THE SAMPLE

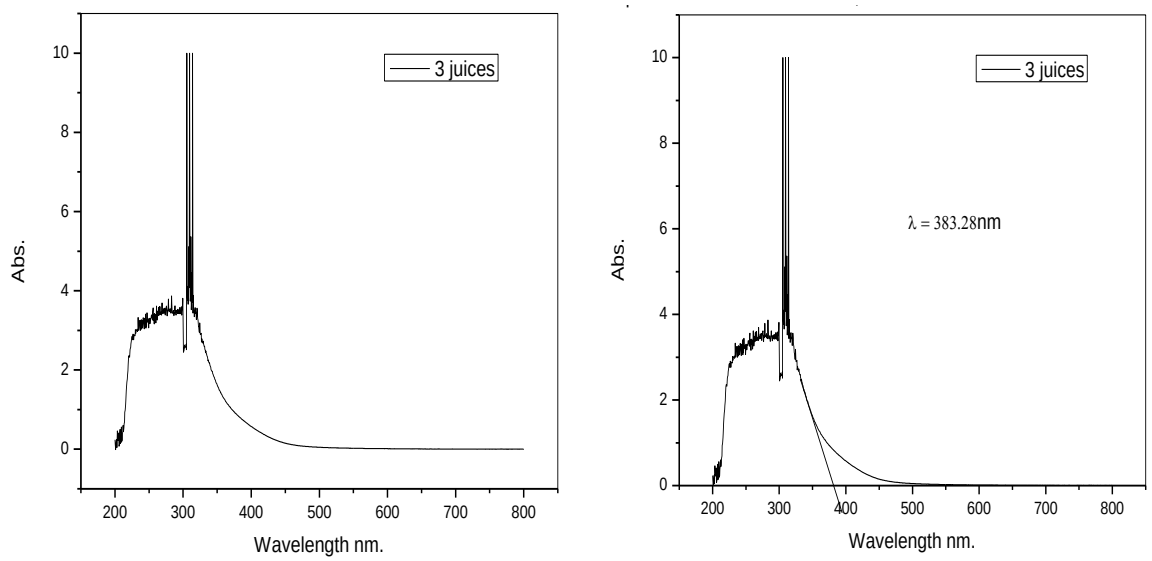

Figure 8. The graph is plotted against absorbance versus wavelength for UV – Vis Characterization.

UV absorption is usually shown by C-dots prepared using various techniques but still the positions of absorption peaks of UV are entirely different for different techniques for preparation of C-dots. Energy gap and refractive index of CDs from different precursors can be obtained from UV – Vis Spectrophotometer using liquid sample, when the sample undergoes characterization, we get few values which is plotted as absorbance versus wavelength. The peak lies at 383.28 nm as shown in figure(8). By knowing wavelength, we can find Energy gap, by knowing the value of the energy gap refractive index is calculated. We can classify precursors into different types of materials based con energy gap obtained.[8]

Energy gap formula, $E_g = \frac{hc}{\lambda} = \frac{6.626\ X\ 10^{-34} X\ 3\ X\ 10^{8}}{383.28\ X\ 10^{-9}}$ = 5.186 X10^{-19} J = 3.241eV

Energy gap of sample is found to be **3.241eV.** Refractive index, n = 4.084 – 0.62 E_g, = 4.084 – 0.62 X 3.241 , n = 2.0745.

Refractive index of sample is found to be **2.07458.**

In case of conductors, band gap $E_g \sim 0$ eV. Where as in case of insulators, $E_g \sim$ 3-4 eV. So, band gap in case of semiconductor is of order $E_g \sim 1$ eV. As per this data the above sample is Insulator.

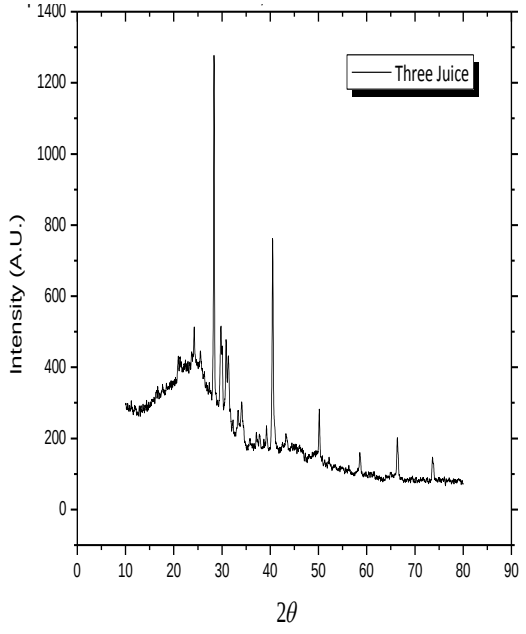

Figure 9.

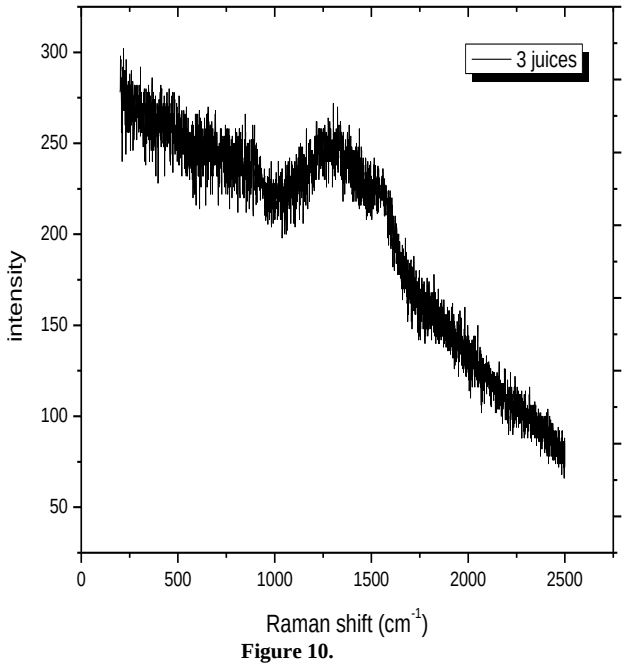

Figure 10.

Figure 9. The graph is plotted against intensity versus 2θ for XRD Characterization.
Figure 10. The graph is plotted against intensity versus Raman shift(cm^{-1}) for Raman Characterization.

The XRD patterns of CDs were obtained by using XRD spectrometer using powder sample by this characterization, we can find out the nature of the material. The graph is plotted against intensity versus two theta. For sharp peak the material may be taken as crystalline. For broader peak it maybe polycrystalline, while in case where there is no peak, but some noisy pattern, then the material is said to have amorphous nature. So as shown in the figure (9) it is having sharp peaks, then it indicates that the sample is of crystalline nature. The various structures of

the C-dots were also examined. Therefore, it demonstrates wide Range peak. [9]
The CDs of different precursors are obtained from Raman characterization using powder sample. From, this characterization we can find the functional group of the CDs based on their peaks obtained in graph which is plotted against intensity versus Raman shift as shown in figure (10). The peaks are in the region 1000 – 1250 cm^{-1} having functional group υ(C=S) and it is Raman strong and IR weak and Another region is around 1400-1470 cm^{-1} δ(CH2) δ(CH3) asym and it is Raman medium and IR medium. [10,28,29,30]

Under FTIR Characterization the sample is Indicated as two regions finger print and Group and identifying functional Group.

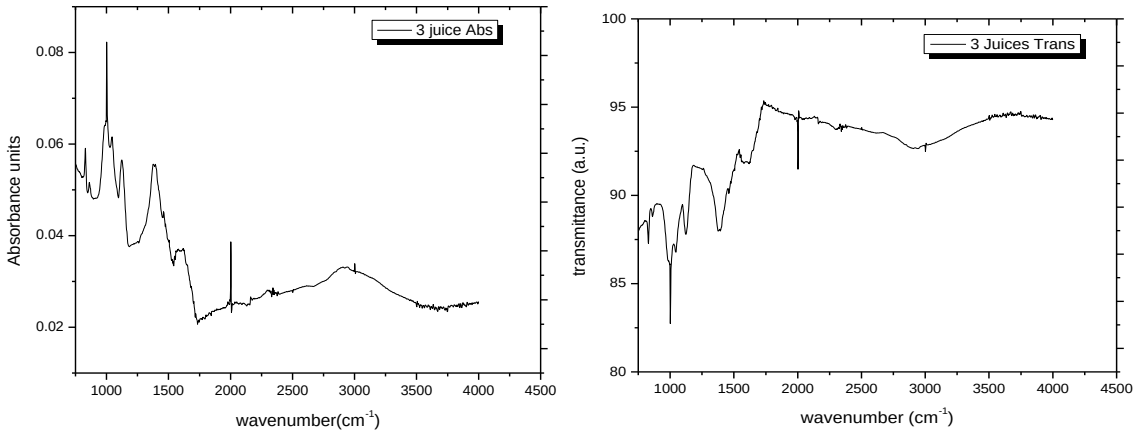

Figure 11. The graph is plotted against absorbance versus wave number (cm^{-1}) and another graph is plotted transmittance versus wave number (cm^{-1}) for FTIR Characterization.

The surface functional groups of CDs obtained from different precursors were identified by using FTIR spectroscopy by powder sample. Based on the classification of the wavenumber as shown we identify the sample. The peaks at 1000 and 2000 cm^{-1} so as shown in the figure (11). The peak at 1000 cm^{-1} is in finger print region having single bond. The graph is plotted against absorbance versus wave number (cm^{-1}) and another graph is plotted transmittance versus wave number (cm^{-1}). [11,12, 28,29,30]

SAMPLE KEPT UNDER UV ILLUMINATOR TO CHECK THE PRESENCE OF CDs

Figure 2. Long UV (320nm-400nm)

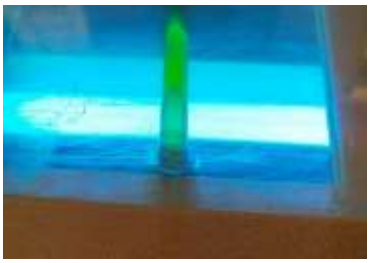

Figure 3. Mid UV (255nm-312nm)

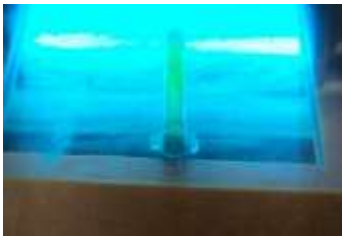

Figure 4. Short UV (100nm-254nm)

Figure 5. Day light (500nm)

After the preparation of sample, it is kept under UV illuminator to check the presence of the carbon dots by passing the different wavelengths. Sample is kept under 4 different types of wavelengths, long UV having wavelength of 320nm-400nm, Mid UV 255nm-312nm, short UV 100nm – 254nm and in day light 500nm. When UV light is allowed to pass through the sample it emit Green Color as shown in above figures, which shows the presence of CDs.

SAMPLE PREPARATION PICTURES

Figure 6. Solution of Lemon, Onion Papaya juice.

Figure 7. Powder sample after heating in a muffle furnace.

As mentioned in synthesis of CDs above are the pictures of the sample after preparation. Figure 6 indicates liquid sample and Figure 7 indicates powder form of sample after heating in muffle furnace.

CONCLUSION

In this project work, detail study related carbon dots and its synthesis in various methods are done using natural precursors. The synthesized Samples are 3 Precursors (Papaya + Lemon + Onion) are successfully synthesized by Bottom – up Approach using green synthesis method. After the synthesis, the sample is kept under UV illuminator to check the fluorescence property. It also conforms the production of dots. Later, the samples are characterized for UV, XRD, RAMAN and FTIR successfully.

Declaration by Authors

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Conflict of Interest: The authors declare no conflict of interest.

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