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Green Synthesis of Multipurpose Carbon Quantum Dots

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Abstract

Carbon quantum dots (CQDs) is a rising star of carbon nanomaterial, by virtue of their unique chemical, optical and electronics properties. Luminescent carbon quantum dots (CQDs) represent a new form of carbon. Nano material which have gained widespread attention in recent years, especially in chemical sensors, bio imaging, solar cells, light emitting diodes (LEDs) and electro catalysis.

The carbon quantum dots (CQDs) can be prepared using various methods. The aim and objectives of the current study are to synthesize multipurpose carbon quantum dots via eco- friendly raw materials and hydrothermal technique.

To synthesize carbon quantum dots (CQD's) using hydrothermal method via green approach. To characterize the prepared samples by X-ray diffraction (XRD) for structural determination. To characterize the prepared samples by Transmission electron microscopy (TEM) and by Infrared spectroscopy (FTIR).To investigate the optical characteristics using UV-Vis spectroscopy and the fluorescence Characteristics of the prepared CQD's. Depending on the obtained properties materials can be used for suitable application inoptoelectronics devices or biomedical applications.

Keywords: Carbon Quantum Dots, XRD, TEM, FTIR, CQD's

Introduction

The carbon quantum dots (CQDs) can be prepared simply by multiple techniques such as Hydrothermal Method, Microwave pyrolysis, Arc discharge method, electrochemical synthesis etc. Carbon quantum dots (CQDs) were first discovered during the study of single walled carbon nanotubes in 2004 by Xu et al. Later in 2006 CQDs have been invented widely as a new member of quantum dot family. Carbon Quantum dots (CQDs) are also called as Carbon dots (CD or C-Dots) or carbon nano dots (CNDs) are also a novel class of carbon nanomaterial with prominent carbon nanoparticles with ultrafine sizes 10 nm.

Physical and chemical properties: Absorbance: Generally, the optical absorptionpeaks of CQDs in the UV-visible region is usually estimatedas π-π ∗transition of sp2 conjugated carbon and n-π ∗ transition of hybridization withhetero atom such as N, S, P, etc. The absorption property can be manipulatedthrough surface passivation or modification process. Developed a facile hydrothermal method to synthesize red, green and blue luminescent CQDs by usingthree isomers of phenylene diamines. [12] The UV-visible absorption spectraas-obtained CQDs exhibited analogous pattern. Interestingly, the absorptiontransitions of these three CQDs were red-shifted, indicating the electronicband gaps of the CQDs were smaller than their corresponding precursors.

Photoluminescence

In general, one uniform feature of the PL for CQDs is the distinct dependence of the emission wavelength and intensity. The variation of particle size and PL emission can be reflected from the broad and excitation-dependent PL emission spectrum studied the emission behaviors of CQDs under an irradiation at 470 nm wavelength with various concentrations. It was found that the PL strength of the CQDs solution first increased and then decreased as the concentration increased. [15]

Methodology

Since the discovery of CQDs, a large variety of techniques for the preparation of CQDs have been developed [23]. Generally, synthetic methods of CQDs can be clarified into two groups: top-down and bottom up methods. In top-down process, the macromolecule is destroyed or dispersed into small-sized CQDs by physical or chemical methods; while the bottom-up approach mainly refers to the polymerization and carbonization of a series of small molecules into CQDs through chemical reaction [23].

Hydrothermal/ Solvo Thermal Synthesis

The hydrothermal method for nano structure synthesis is of considerable interest for practical applications since it is a low cost, environmentally friendly technique which can be used on large area and/or flexible substrates, as well as fabrication of free-standing nanostructures. It usually does at a high vapor pressure level and using a high-temperature aqueous solution; hence it is termed as ‘Hydro’ + ‘Thermal’ = Hydro thermal method. We have observed natural process for more than 800 years now and the term has geological origins. [10]

It is a specific style of strong vessel that we intend to face up to high temperatures and better pressure levels from within. [22] As many hydrothermal processes need to use solutions

having a corrosive impact on the interior material of the autoclave. Also, we apply special protective coating stop or prevent corrosion or part of it.

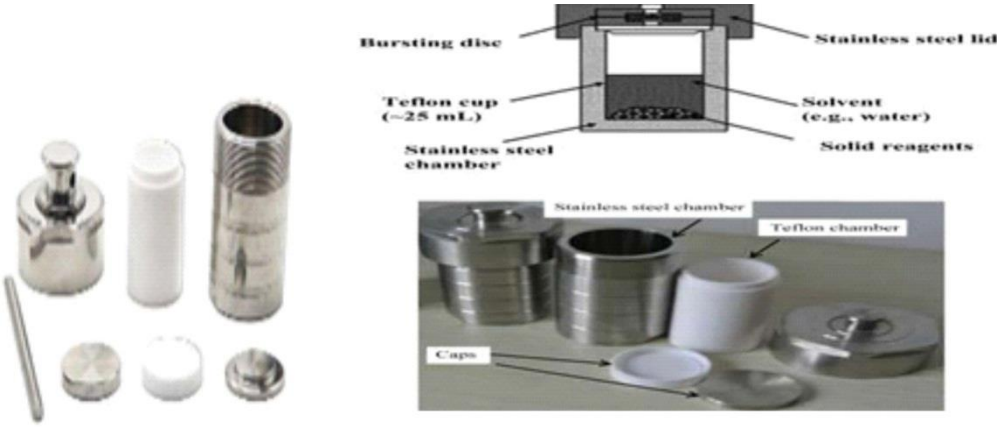


Fig.:Instrumentation required for hydrothermal method and auto-clave for hydro-thermal technique

Advantages Of Hydrothermal Synthesis Method For Nanoparticle Synthesis

1. Able to produce crystalline phases which aren't stable at higher temperatures safely.
2. Grows materials which are known to have a higher vapor pressure as their melting point gets closer.
3. Creates larger-sized and high-quality crystals and nanoparticles, with control over their content and composition.

In particular, hydrothermal method is one of the most commonly used procedurein CQDs synthesis, because the setup is simple and the outcome particle is almost uniform in size with high QY. In a typical approach, small organic molecules and/or polymers are dissolved in water or organic solvent to form the reaction precursor, which was then transferred to a Teflon-lined stainless steel autoclave. The organic molecules and/or polymers merged together at relatively high temperature to form carbon seeding cores and then grow into CQDs with a particle size of less 10 nmreported the highest QY of CQDs up to about 80%, which is almost equal tofluorescent dyes. [26] Hydrothermal synthesis is one of the most commonlyused methods for preparation of nanomaterial.To control the morphology of the materials to be prepared, either low-pressure or high-pressure conditions can beused depending on the vapor pressure of the main composition in the reaction.

New synthesis methods, for example, microwave-assisted hydrothermal synthesis and template-free self- assembling catalytic synthesis, are reported in this special issue[15]. Research work on optimization of the synthesis conditions is included as well.

Synthesis Of COD's: Raw Materials Used

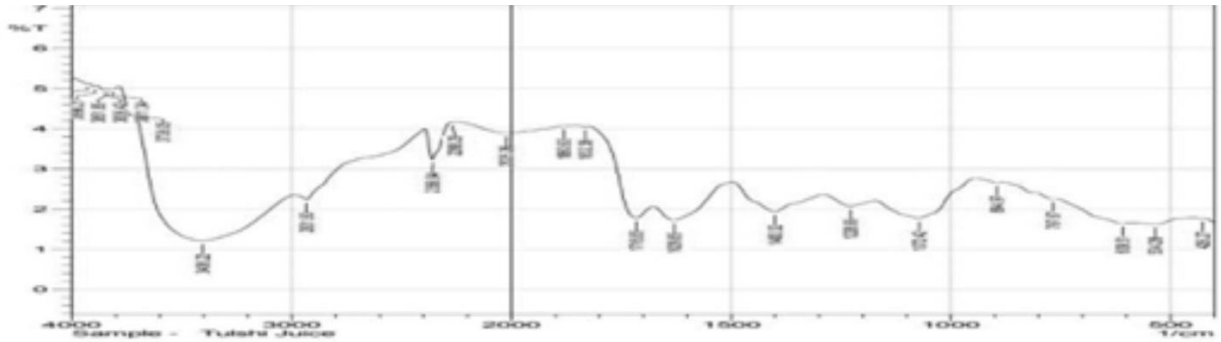
1. Saccharum officinarum (Sugarcane) baggase pulp.
2. Ocimum sanctum (tulsi) and 3. Citrus X sinensis. (Orange juice).

Procedure

Newly sugarcane bagasse pulp was collected from local market juice shop, it was waste so easily available material all time. The pulp was washed and cleaned with deionized water. Pulp was dehydrated in sunlight for three days before being ignited. The citric acid and ammonia was added briefly, 3\2 gm of yielded carbon and 2 gm of citric acid was homogeneously mix with 25ml distilled water, then the ammonia was add to precursor to set the pH. The isolated precursor was completely shifted to autoclave at stable temperature of 160 C for 5\6 hrs. Then the reactive mixture solution was ultra sonicated for 1hrs and then centrifuged for 60min to remove superior un-dissolve particles.

1. Ocimumsanctum (tulsi) stem was collected, it was easily available material all time. It was crushed before and after ignition briefly, 1\2 gm of yielded carbon was homogeneously mix with 25 ml distilled water, then the ammonia was added to precursor to set the pH. The isolated precursor was completely shifted to autoclave at stable temperature of 160 C for 5\6 hrs. Then the reactive mixture solution was ultra sonicated for 1hrs and then centrifuged for 60 min to remove superior un-dissolve particles.
2. Orange fruit juice was collected; it was easily available material all time. It was washed before, then the juice from orange was collected and filtered. Briefly, 20ml of yielded carbon, the isolated precursor was completely shifted to autoclave at stable temperature of 160 C for 5\6 hrs. Then the reactive mixture centrifuged for 60 min to remove superior un-dissolve particles.
3. Characterization: FTIR :Fourier transform Infrared (FTIR) spectroscopy is a versatile technique for the characterization of materials belonging to the carbon family. Based on the interaction of the IR radiation with matter this technique may be used for the identification and characterization of chemical structures. Most important features of this method are: non-destructive, real-time measurement and relatively easy to use. Carbon basis for all living systems has found numerous industrial applications from carbon coatings (i.e. amorphous and nano crystalline carbon films: diamond- like carbon (DLC) films) to nanostructured materials (fullerenes, nanotubes, graphene) and carbon materials at nano scale or carbon dots (CQD's).UV-V: is a fast, simple

and inexpensive method to determine the concentration of an analyte in solution. In UV-V, a beam with a wavelength varying between 180 nm and 1100 nm passes through a solution in a cuvette.



Result And Discussion

Analysis of Saccharum officinarum (sugarcane bagasse pulp):

: 1 FTIR

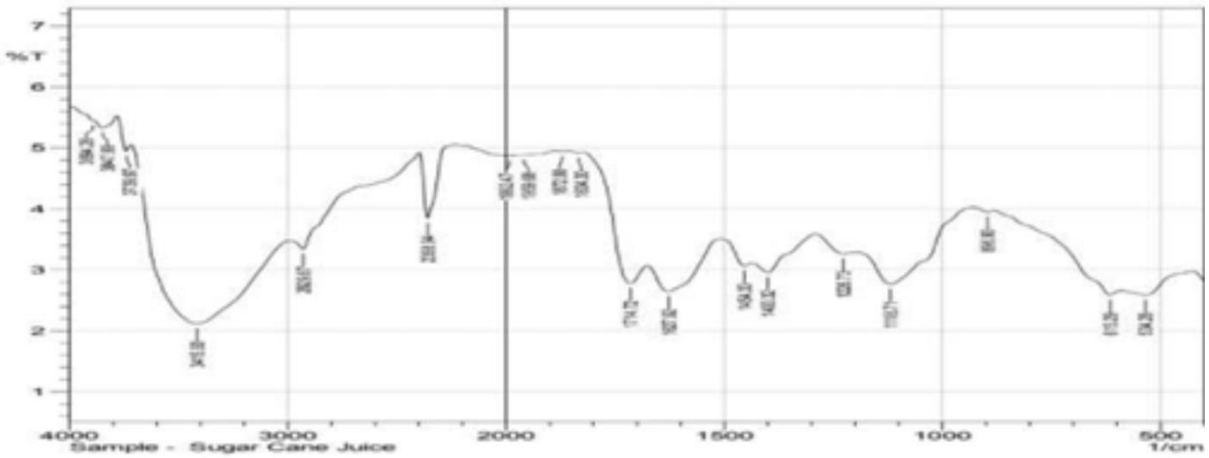


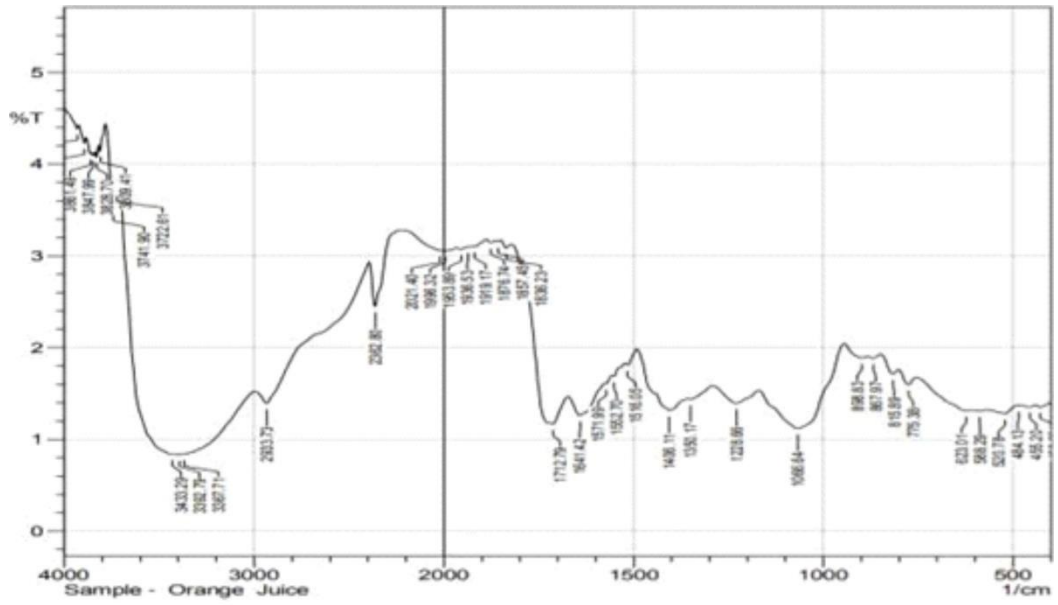
Fig. :FTIR for Saccharum officinarum (sugarcane baggase pulp)

Above FTIR spectrum showing that absorption peak at 3415.93 cm-1 is related to O-H / N-H and a sharp peak at 2358.87 cm-1 corresponds to methyl group (C-H) group. The peaks nearly 1627 cm-1 and 1400 cm-1 corresponds to C=O and COO- functional group respectively. The presence of these functional group plays a vital role in strengthening antibacterial effect of prepared CQDs.

For ocimum sanctum, Fig. FTIR for ocimum sanctum (tulsi)

Above FTIR spectrum showing that absorption peak at 3321.93 cm-1 is related to O-H / N-H and a sharp peak at 2931.87 cm-1 corresponds to methyl group (C-H) group. The peaks nearly 1627 cm-1 1687 cm-1 and 1400 cm-1 corresponds to C=O and C=C stretching functional group respectively. Citrus X Sinensis (Orange juice), Fig. FTIR for Citrus X Sinensis (orange juice)

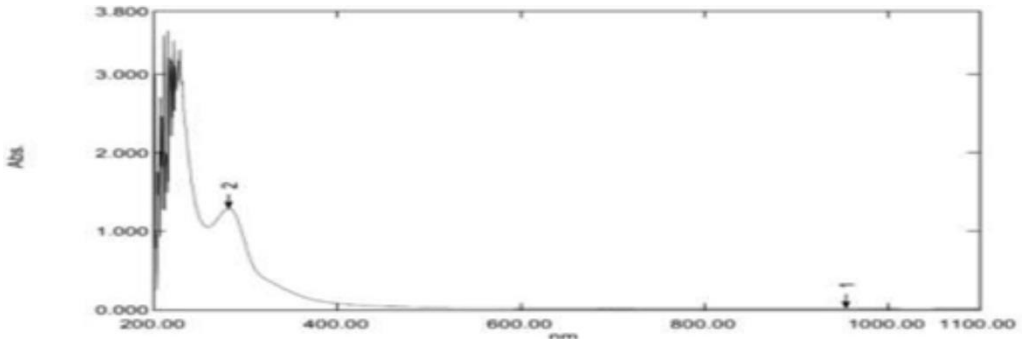
Above FTIR spectrum showing that absorption peak at 3433.23 cm-1 is related to O-H / N-H and a sharp peak at 2362.87 cm-1 corresponds to methyl group (C-H) group. The peaks nearly 1712 cm-1 1516 cm-1 and 1406cm-1 corresponds to



C=O and C=C stretching functional group respectively.

2.UV- Visible spectroscopy Analysis

1. **Saccharum officinarum (Sugar cane) bagasse pulp :**Fig. (a) UV-Vis Saccharum Officinarum(Sugar cane bagasse pulp). The UV – Visible spectrum of prepared CQDs is given above. The spectrum displays two corresponding peaks 282 nm and 332 nm in a supernatant solution of carbon quantum dots. The diluted CQDs show an intense greenish color upon illumination by UV light.



2. **Ocimum sanctum (tulsi) :**

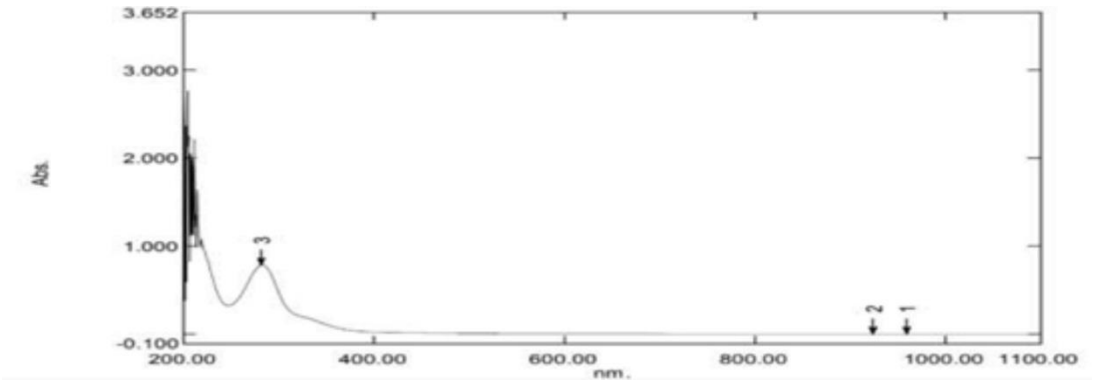


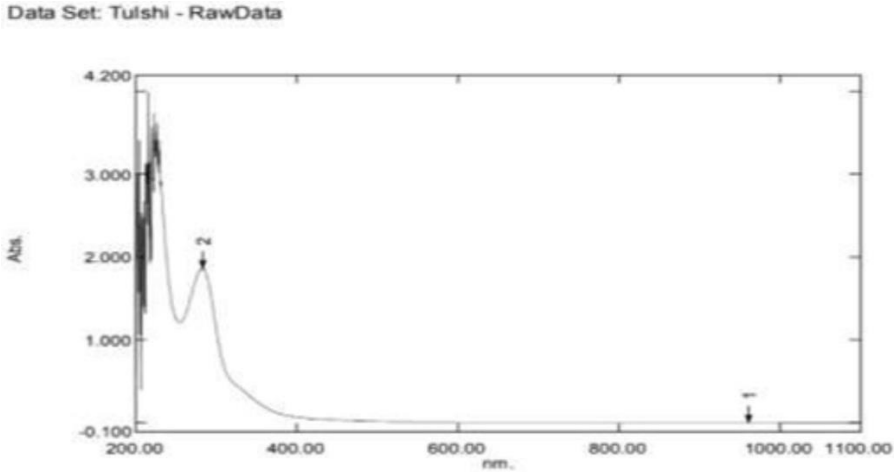
Fig. (b) UV-V is The UV – Visible spectrum of prepared CQDs is given above. The spectrum displays ir-responding peak 282 nm. is Ocimum sanctum (tulsi)3-Citrus X Sinensis (Orange juice) Fig. (c) UV-Vis Citrus X Sinensis (orange juice).

The UV – Visible spectrum of prepared CQDs is given above. The spectrum displays corresponding peak 280 nm. The prepared CQD's samples fluorescence emission was observed under UV lamp of 254 nm280 nm. The CQD's obtained using orange juice precursor exhibits green emission. However,

CQD's obtained using sugarcane and Ocimum sanctum precursors exhibits light green emission.

Conclusions

The carbon quantum dots (CQDs) were synthesized by theHydro thermal method. A simple direct green synthesis approach was used utilizingocimumsanctum (tulas), Saccharum officinarum (Sugar cane baggase) pulp and CitrusX Sinensis (orange juice).FTIR analysis confirms the formation of carbon-basedmaterial formation. The spectrum displays two corresponding peaks 282 nm and 332nm in a supernatant solution of carbon quantum dots for sugar cane precursor.



The UV – Visible spectrum of prepared CQDs is given above. The spectrum displays corresponding peak 282 nm for ocimum sanctum juice precursor. The spectrum displays corresponding peak 280 nm for orange juice precursor. The prepared CQD's samples fluorescence emission was observed under UV lamp of 254 nm - 280 nm.

The CQD's obtained using orange juice precursor exhibits green emission. However, CQD's obtained using sugarcane and Ocimum sanctum precursors exhibits light green e mission. The obtained properties can be used for opto-electronic devices and biomedical applications.

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