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ORIGINAL PAPER

Synthesis of Carbon Dots from Kitchen Waste: Conversion of Waste to Value Added Product

A. L. Himaja · P S. Karthik · B. Sreedhar · Surya Prakash Singh

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Abstract Synthesis of Carbon dots (C-dots) from biodegradable waste is a much researched subject now-a-days. The demand for green chemistry and cost-effectiveness lead us to synthesize C-dots from kitchen waste. Nanometer sized carbon particles with unique optical properties were observed during the study. A simplistic approach was used for the synthesis which converted the waste materials into value-added products. Several different analyses were carried out on the obtained product which showed pristine results in comparison with the previous results.

Keywords Carbon nanomaterials · Carbon dots · Green chemistry · Bio-compatible · Fluorescence

Introduction

Highly fluorescent Carbon nanomaterials with sizes less than 10 nm are called carbon dots which belong to the carbonaceous family. These were first discovered in the year 2004 and grabbed the attention of many researchers because of their high fluorescent property. They were inadvertently discovered while electrophoresis of single walled nanotubes [1]. Scheme 1

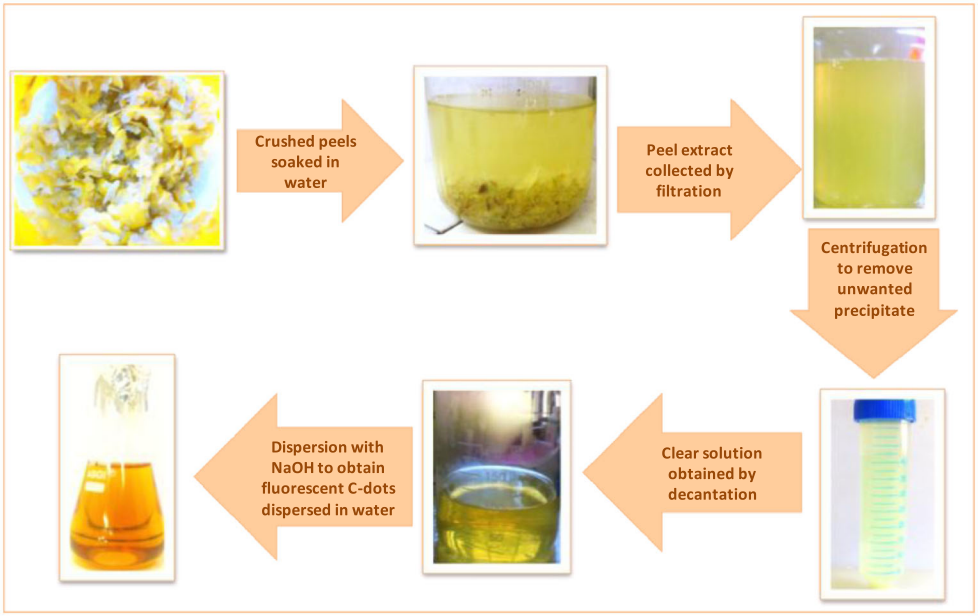
C-dots are of much interest compared to traditional quantum dots, as they are considered to be bio compatible and cost effective [2]. Carbonization of glucose, sucrose, glycerol, citric acid, ascorbic acid, etc. was used for the production of C-dots [3, 4]. But it was a very sophisticated and time consuming approach. They have also been synthesized from carbonaceous materials like graphite and carbon nanotubes by physical methods like laser ablation [7], microwave synthesis [4, 8], ultrasonic treatment [9, 10], arc discharge [1], plasma treatment and chemical methods like electrochemical oxidation, thermal oxidation, and vapor deposition of soot [5], wet chemical and electrochemical method [11–13].

C-dots have also been synthesized from commercially available food caramels like bread, sugar, jaggery etc. [21]. Due to the presence of carbohydrates in these food products, C-dots could be easily obtained. They were even synthesized from coffee grounds which were used and dried [22]. This leads us to a conclusion that rather than using physical methods, greener methods could be used for unsophisticated synthesis of C-dots.

Green chemistry is an approach that paves the way towards sustainable processes by minimizing the waste produced. Usage of non-toxic starting materials, environment friendly chemicals is the primary motto of using this process. The results produced are thus biocompatible in nature. Green synthesis of C-dots is highly desirable as it is less time consuming and doesn't require higher temperatures [14, 15]. C-dots produced by these methods are of high yield and cost effective. Carbon can be found both in organic and inorganic materials, which are readily available for a simplistic approach to synthesize C-dots [16–20]. In recent times, several groups have been reported to achieve success in green synthesis of C-dots by hydrothermal treatment from many organic materials like orange peel [17], sugar cane bagasse [18], banana juice [16], sugar cane juice [19], Trapabispinosa peel [20] etc., which are abundantly available. The end product obtained was of high yield and the process was very less time consuming.

Size and yield of the C-dots can be altered by differing the starting materials and duration of the treatment. There are many reports on the size of C-dots which show that they lie in the nanometer range [1–11, 16–20]. An example includes,

A. L. Himaja · P. S. Karthik · B. Sreedhar · S. P. Singh (✉)
Inorganic and Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, Uppal road, Tarnaka, Hyderabad 500007, India
e-mail: spsingh@iict.res.in



Scheme. 1 Step-wise procedure for green synthesis of C-dots from kitchen waste

C-dots prepared by surface passivation using PPEI-EI (propionylethylenimine-co-ethylenimine) showed feature sizes of less than 5 nm. Surface passivation of C-dots is necessary in some cases for improved fluorescence.

C-dots derived from candle soot were sp^2 hybridized. The chemical composition of the purified C-dots was found to be 36.8 % C, 5.9%H, 9.6 % N, and 44.7 % O, due to the presence of carbonyl groups. They are basically oxygenous nanoparticles with size less than 10 nm [5].

C-dots are now-a-days considered to be superior materials for application in bio imaging, bio sensing, drug delivery, optoelectronics, solar cells and photovoltaic devices due to their unique properties like photoluminescence, high water solubility, chemical inertness, less toxicity, high yield etc. [22–31]. Quantum dots have been used in bio imaging since many years but toxicity concerns have led to the replacement of quantum dots with C-dots [32]. C-dots are composed of intrinsically non-toxic elements which allow them to be used in bio analytical tools. C-dots are said to have very low cytotoxicity and were shown to internalize cells, probably by endocytosis mechanism. A recent study showed the coupling of C-dots with plasmonic metal nanoparticles which resulted in improved brightness and photostability of C-dot. This helps in better detectability in bioanalytical applications. Organic optoelectronics are more preferable compared to inorganic versions as they are cheaper to make. Further improvement in efficiency is necessary to meet the requirements for commercialization of this technology. C-dot supported silver nanoparticles have been reported which showed improved efficiencies in polymer light emitting diodes and polymer solar cells [30]. The surface Plasmon resonance effect of these nanoparticles allowed significant radiative emission and light absorption which led to improved efficiency.

Another application of C-dot includes optical fibers. Optical sensing is an important analytical technique widely used in the field of biomedical and chemical sciences. The combination of optical fiber technology with fluorescent C-dots results in improved sensitivity and fast response time. C-dots were immobilized on optical fiber head using sol–gel technique. The sensor selectively and reversibly responded to mercury (II) ions by a quenching mechanism. The response of the nanosensor was fast (less than 10 ns) and stable. C-dots have also been used in the fabrication of white LEDs which produced higher brightness [31].

In our work, we present a report on highly fluorescent C-dots which have been synthesized using kitchen waste (fruit/vegetable peel). The synthesis process was based on green chemistry and the starting materials used are easily available, eco-friendly and cost effective as well. The process was carried out at temperatures just above the boiling point of water. The whole process was less time consuming. The obtained C-dots were highly water soluble. Clear yellow suspension of C-dots was observed initially under visible light. They were highly fluorescent when checked under Ultra-violet light and showed green fluorescence. Different characterization techniques like UV/Vis spectroscopy, Photoluminescence spectroscopy, XRD, FTIR, TEM and Micro Raman spectroscopy were performed on the end products.

Materials and Methods

The materials used contained peels of fresh fruits/vegetables such as the fresh Indian yellow cucumber and pineapple. All the experiments were performed using distilled water. NaOH

was used to solubilize C-dots and further improve the fluorescence.

Peels of fresh cucumber/pineapple were taken and washed thoroughly with water. Peels were then crushed into a paste using a home-use mixer grinder. The cleaned peels were directly taken in a jar and then ground into a fine paste without the addition of water. The consistency of the paste was kept very thick. The peel paste obtained was very fine and gooey. It was purposely made into a fine paste so that the material when mixed in water gets completely dispersed and we could extract the maximum carbon content present in the peels. If the consistency of the paste changes or if the peel paste was flaky in texture, the possibility of extracting the carbon content present in the peels will be reduced and thus there will be a reduction in the amount of C-dots extracted. Hence, we opted to prepare a very thick and fine paste.

The next step was to mix about 50grams of peel paste in 250 ml of distilled water. This mixture was then heated at 150 °C for 2 h and filtered using a regular home-use tea filter resulting in a yellow colored solution. No other filtration technique was opted as the fibrous material that was left out after the dispersion of peel paste in water could be simply removed by using a tea filter. The solution was then centrifuged at 4500 rpm for 20 min to remove any heavier particles present. Then, 100 ml of the solution was taken by decantation. The former was a clear pale yellow colored solution. The solution was then refluxed at 150 °C for 2 h and later allowed to cool down naturally. It was then centrifuged at 4500 rpm for 20 min. The former was then suspended with 1 N 5 ml NaOH. A clear and bright yellow suspension of C-dots was obtained which showed green fluorescence when checked under UV light. The fluorescence intensity varied for different starting materials.

The size of C-dots can be tailored by changing the parameters like temperature, consistency of peel paste and centrifugal speed. The above method was repeated by variations in these parameters which resulted in larger sized C-dots. The parameters mentioned above have been optimized to obtain a clear dispersion of C-dots ranging in the nanoscale without the presence of any larger particles. For low temperatures and low centrifugal speeds, completely dispersed C-dots were not produced and solid particles were left out in the solution which resulted in large sized impurities. For higher temperature and higher centrifugal speeds, the fluorescence property got reduced. Thus, we have produced a clear dispersion of C-dots in water by following an optimum procedure.

A schematic shown below depicts the procedural details in a step-wise manner. Similar procedure was followed for both the peels taken with slight variations in the parameters according to the kind of peel used.

Results and Discussion

Our motto in this experiment was to synthesize C-dots with the use of kitchen waste materials and an easy synthesis technique. As a result we could obtain C-dots with easily available materials and simple apparatus.

The end products obtained showed significant results which were in good acceptance with the previous reports [16–20]. The water soluble C-dots obtained from two different peels namely cucumber and pineapple showed difference in results. Comparatively, we found that the C-dots extracted from cucumber peel showed better results. Also, the stability observations showed that C-dots obtained from pineapple peel degraded soon within few weeks whereas C-dots obtained from cucumber peel were highly stable with very less precipitation. The precipitation could be removed by centrifugation of the product. Fungal formation was observed on the sample of C-dots obtained from pineapple peel whereas the C-dots obtained from cucumber peel did not show any such activity and remained as a clear bright yellow liquid for several months. Both the samples were preserved in a refrigerator at about 3 °C temperature. Hence, the comparative results show that the C-dots synthesized from cucumber peels were much better and could be potentially applied in the fields of organic electronics and bio-imaging.

UV/Visible Spectrometry

UV-Visible absorption spectra were performed by using SICAN2600 spectrometer. The as-prepared C-dots were characterized for UV–vis absorption spectrum which is shown in Fig. 1. The C-dots obtained from cucumber peel were observed to have two absorption bands at 267 nm and 328 nm. UV-visible absorption peaks occurred at 317 nm and 269 nm for C-dots obtained from pineapple peel.

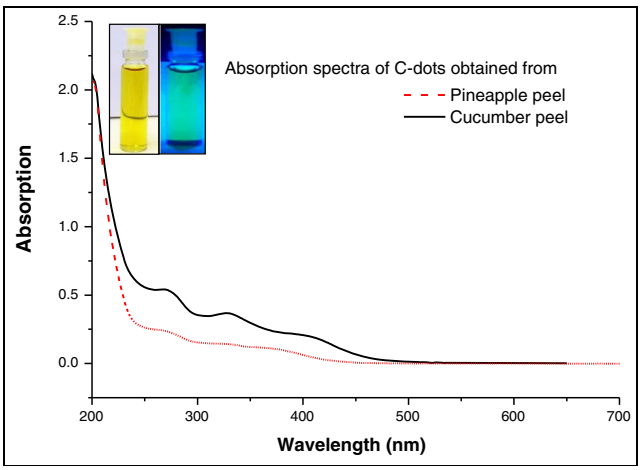


Fig. 1 UV-visible absorption spectrum of C-dots prepared from cucumber peel and pineapple peel

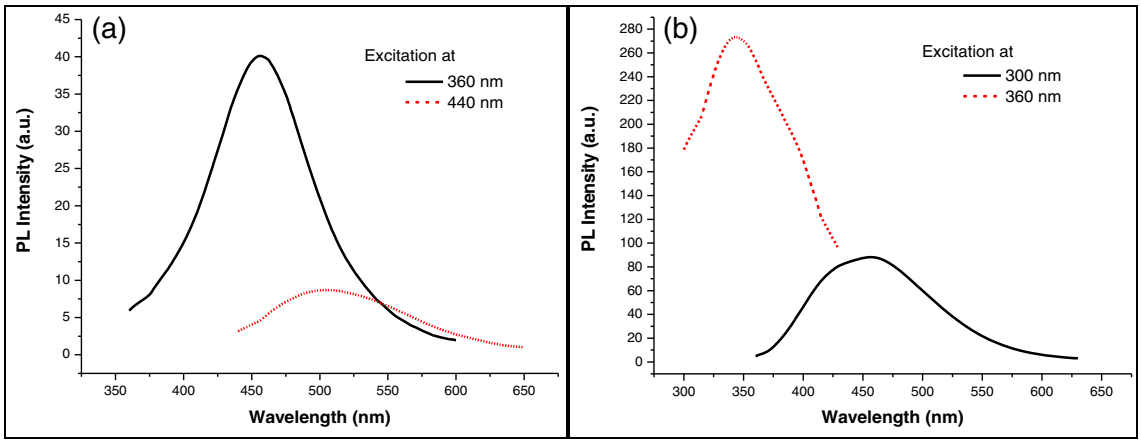


Fig. 2 Fluorescence intensity of C-dots derived from (**a**) Cucumber peel, (**b**) Pineapple peel

Fluorescence Spectrometry

Fluorescence spectra were obtained using Cary Eclipse instrument. All the spectral details were obtained from liquid C-dot samples finely dispersed in water. The intensities were recorded at different wavelengths. UV-Visible range was used for the excitation of the samples. Different excitation wavelengths of 300 nm, 360 nm and 440 nm were used for which the material exhibited emissions ranging in the blue-red wavelength range.

As seen in Fig. 2 (a), the maximum emission for C-dots obtained from cucumber peel was recorded at 502 nm for an excitation wavelength of 440 nm. Similarly, for C-dots

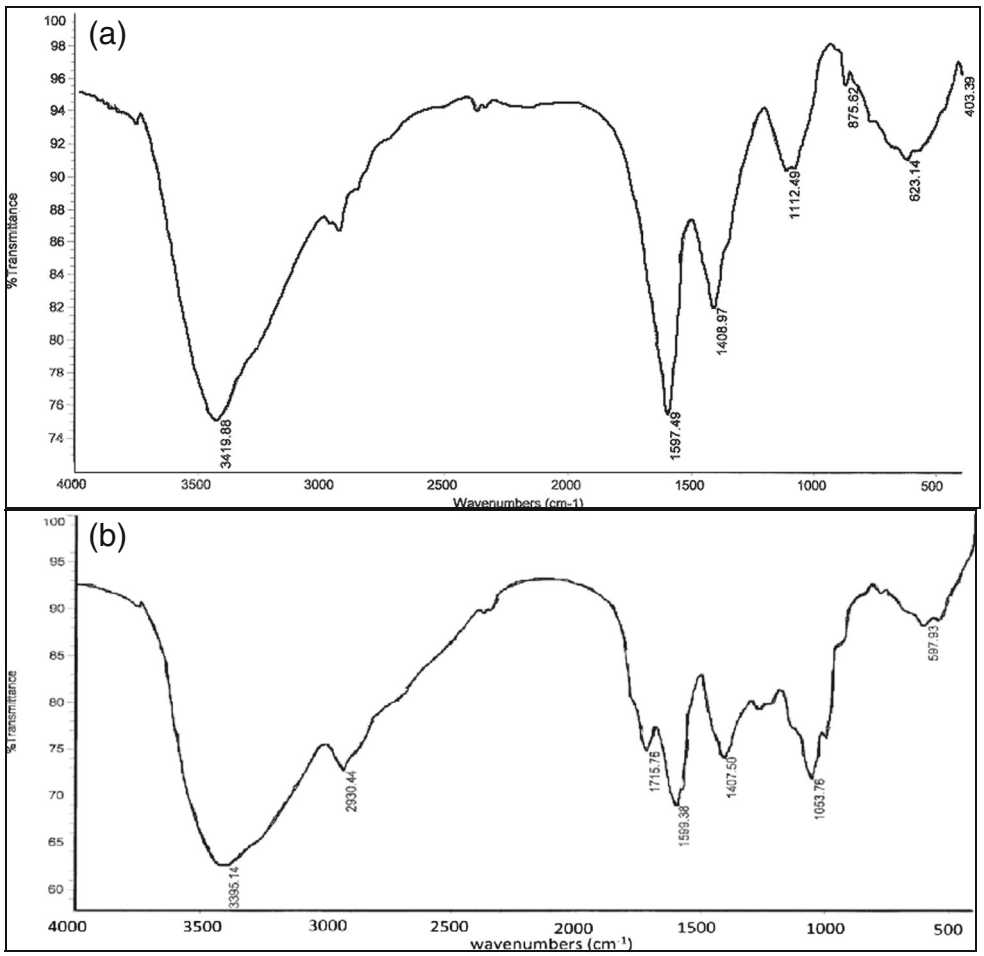


Fig. 3 FTIR spectrum of C-dots prepared from (**a**) cucumber peel, (**b**) pineapple peel

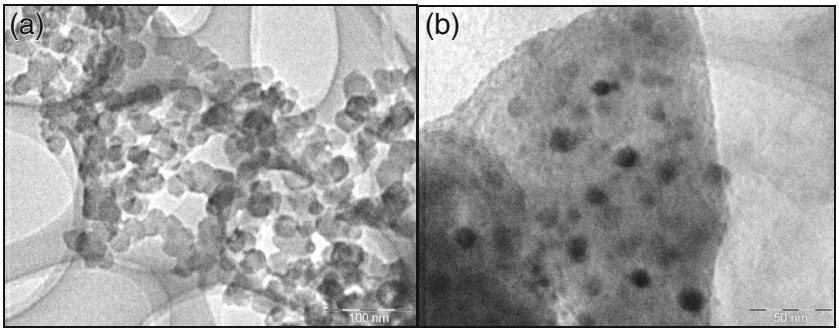


Fig. 4 TEM image of C-dots obtained from (**a**) cucumber peel, (**b**) pineapple peel

obtained from pineapple peel as seen in Fig. 2 (b), the maximum fluorescence emission was recorded at 487 nm at an excitation wavelength of 360 nm. Several reports indicate that the variation in PL intensities is mainly due to the size difference in C-dots. The spectra with higher intensity indicate the presence of large number of smaller particles which were excited at UV-Visible range. These results indicate the presence of different sized particles which showed difference in fluorescence emission for different excitation wavelengths. The determination of excitation wavelengths correspond to the absorption spectra shown in Fig. 1. As the absorption spectra covered the spectral range from 200–500 nm, different excitation wavelengths of 300 nm, 360 nm and 440 nm were chosen as the fluorescence emission exhibited was good enough at those points.

Fourier Transform Infrared Spectrometry (FTIR)

FTIR analysis was performed using Thermo Nicolet Nexus 670 spectrometer at a resolution of 4 cm^{-1}. The sample was dried on a glass plate at 150°and then collected in powdered form and KBr was used as the condition of analysis. Fig. 3 (a) & (b) show the FTIR spectrum of C-dots which was used for identification of functional groups present. As seen in Fig. 3 (a), the C-dots obtained from cucumber peel exhibited a strong characteristic absorption at 3419.88 cm^{-1} which was due to O-H stretching. Another medium stretch was observed at 1597.9 cm^{-1} and also at 1408.87 cm^{-1} which indicated the presence of C-C aromatic rings. A small C-O stretch was also observed at 1112.49 cm^{-1}.

As seen in Fig. 3 (b), the FTIR spectrum showed that the C-dots obtained from pineapple peel exhibited a strong characteristic absorption at 3395.14 cm^{-1} which was due to O-H stretching. Another medium stretch was observed at 1599.38 cm^{-1} and also at 1407.50 cm^{-1} which indicated the presence of C-C aromatic rings. A small C-O stretch was also observed at 1053.76 cm^{-1}. All these stretches indicate that the C-dots are highly water soluble in nature.

This data indicates the presence of different functional groups like hydroxyls, carboxyl, and hydrocarbons etc. which help in the attachment of moieties for targeted drug delivery.

Transmission Electron Microscopy (TEM)

The TEM analysis was performed using Tecnai-12 at an accelerating voltage of 20–120 KV. Fig. 4 (a) & (b) show the morphology of C-dots as obtained from the TEM images.

A band of spherical C-dots can be observed in Fig 4 (a). The TEM image also revealed that the particles were completely dispersed in water. The spherical morphology

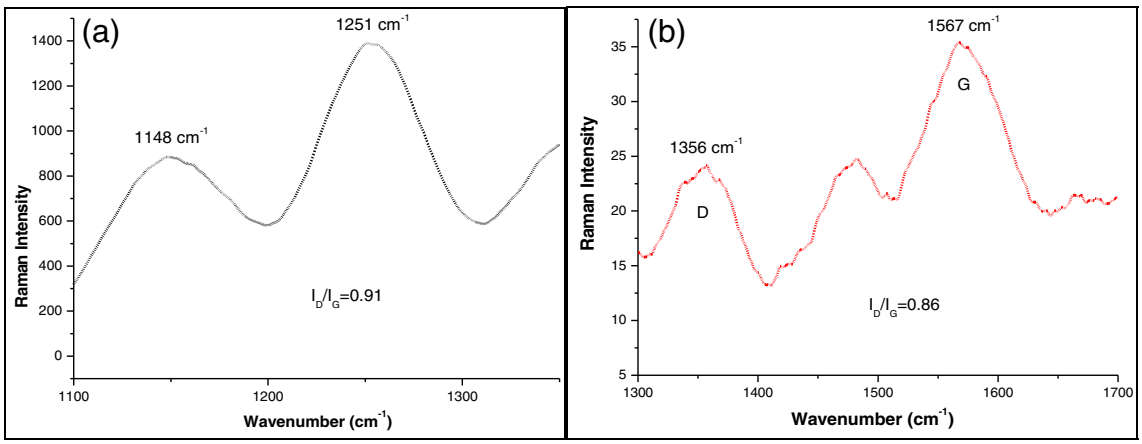


Fig. 5 Raman spectra of C-dots obtained from (**a**) cucumber peel, (**b**) pineapple peel

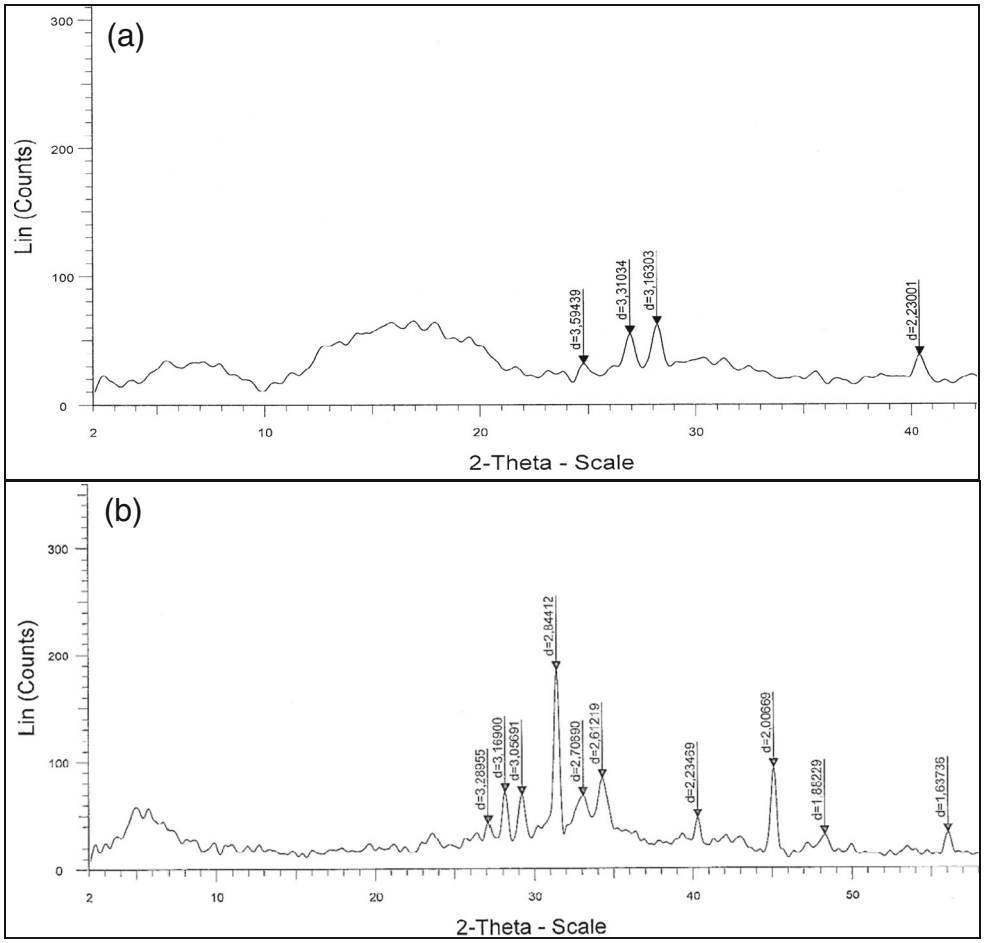


Fig. 6 XRD pattern of C-dots obtained from (**a**) cucumber peel, (**b**) pineapple peel

was clearly visible with the size of C-dots being ~50 nm in diameter. As seen in Fig 4 (b), spherical shaped C-dots were clearly visible with a size of ~50 nm. The TEM analysis was carried out after 2 weeks and the images show the signs of agglomeration of particles. This could be rectified by ultrasonication and centrifugation of the samples.

Micro Raman Spectroscopy

Micro Raman spectroscopy was carried out using Horiba Jobin-Yvon LABRAM HR with a focal length of 800 mm and also equipped with a He-Ne 633 nm Laser and Ar 514 nm Laser. The spectral range varies from 60–5500 cm^{-1}. Finely powdered sample has been used for the purpose of Raman spectroscopy.

As seen in Fig. 5 (a), the G and D bands obtained at 1251 and 1148 cm^{-1} respectively, indicate the presence of both sp^3 and sp^2 hybridization pattern in C-dots. The ratio of intensities I_D/I_G was found to be 0.91 which was slightly higher than the previously reported results. In case of Fig. 5 (b), Raman intensities of G and D bands were recorded at 1567 and 1356 cm^{-1} respectively. The relative area of intensity I_D/I_G was found to be o.86 in this case. These results suggest the presence of two kinds of hybridization in C-dots in comparable amounts.

Powder X-Ray Diffractometry (XRD)

The X-ray Diffractometry was performed using Bruker D8 Advance with lynx-eye detector and power of 2.2KW. The finely dispersed liquid sample was dried on a clean glass plate at 150°C. The sample was then made into a fine powder for the purpose of X-ray diffraction analysis.

Figure 6 (a) & (b) show the XRD pattern of C-dots which have an intense peak at 31.428° and 29.781° respectively. These results indicate the crystalline nature of C-dots which is an improvised result in comparison with the previous studies that show amorphous nature of this material.

Conclusion

Here, we are reporting a simplistic and cost-effective approach for large scale synthesis of C-dots. Kitchen waste which is bio-degradable in nature is a great source for greener synthesis

of carbon nanomaterials. Reusability of vegetable/fruit peels which makes the end product cost-effective has been demonstrated in this paper. Also, the toxicity concerns can be overcome by the use of green chemistry. The novel optical properties exhibited by C-dots help them in building their path towards organic electronic applications. The biocompatibility and non-toxic nature make them highly suitable for application in biology. Drug delivery, bioimaging and bio sensing are the fields where these materials can be applicable. Also, photovoltaic applications have a demand for materials with good charge transfer ability which is satisfied by these C-dots. The new member of the carbon nanomaterial family certainly has a bright future owing to its unique nature.

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