Green synthesis of fluorescent carbon dots through solvothermal treatment of Buchnania lanzan leaves extract

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Abstract: In the present work we have synthesized fluorescent carbon dots (CDs) through solvothermal treatment of Buchnania lanzan leaves extract at 160 °C for 4 h in oven. Here, Buchnania lanzan leaves serve as a renewable source of carbon. The obtained blackish brown CDs solution was centrifuged and the supernatant was filtered through syringe filter (0.22 µm). Further, the CDs solution was dried in vacuum oven to obtain powder. The synthesized CDs were characterized by different techniques including UV-Visible spectroscopy, fluorescence spectroscopy, fourier transform infrared (FTIR), zeta potential, x-ray diffraction (XRD). The as prepared CDs solution was found brownish colored in day light while exhibited green fluorescence under UV light. UV-Visible absorption spectrum displayed characteristic shoulder peaks of CDs at 257 nm and at 356 nm. In the fluorescence spectra, excitation dependent emission behaviour of CDs was seen, which is one of the distinct characteristics of CDs. The negative zeta potential and characteristic peaks in FTIR, suggested presence of carbonyl, amine and hydroxyl functional groups on the CDs surface. XRD spectrum exhibited broad peak at 2θ=19°, suggesting amorphous nature of CDs similar as reported in earlier works. As we have synthesized surface functionalized fluorescent carbon dots from a renewable and abundant precursor, this method can be highly useful in large scale synthesis of carbon dots with reduced costs and will find potential applications in the field of drug delivery, bioimaging, etc.

Keywords: fluorescent carbon dots; solvothermal method; Buchnania lanzan

1. Introduction
Carbon dots (CDs) are an emerging member of carbon nanomaterials [1]. Since its accidental discovery in 2004 [2], CDs have shown numerous potential applications as fluorescent marker, photocatalysts, biosensors, bioimaging, in optoelectronics and in drug delivery [3–5]. In biomedical field CDs have emerged as a promising candidate due to their properties like good 1 aqueous solubility, biocompatibility, tunable optical properties, ease of surface modifications and non-toxic nature [1,4]. The methods of CDs synthesis can be roughly classified into top-down and bottom-up approach [6,7]. Top-down 3 approach involves synthesis of CDs from larger carbon materials. Methods like laser ablation, arc-discharge, chemical oxidation and electrochemical synthesis come under top-down approach. Whereas, bottom-up approach involves CDs synthesis from molecular precursors, which includes methods like microwave treatment, hydrothermal/solvothermal treatment and carbonization [1]. Till now, CDs have been synthesized from numerous precursors using above methods. Unfortunately, most of the earlier methods involve the use of expensive and hazardous chemicals, solvents [8,9]. Therefore, exploration of simple, economic and environment friendly alternate route and starting materials focusing on the green synthesis of CDs is most desirable. In the current work, we have synthesized...
fluorescent CDs by simple solvothermal method using methanolic extract of leaves of *Buchnania lanzan* plant and subsequently characterized them using several techniques. *Buchnania lanzan* (commonly known as Chironji) is a well-known tree of family Anacardiaceae, almost evergreen and found in the tropical deciduous forests of northern, western and central India [10,11]. Methanolic extract of *Buchnania lanzan* leaves is reported to be rich in carbohydrate constituents [12,13] which serves as the carbon precursor for the CDs synthesis. The prepared CDs showed characteristic peaks in the UV-Visible spectrum and exhibited green fluorescence under UV light. Fluorescence Spectra of CDs demonstrated excitation dependent emission behaviour. FTIR result suggests presence of carbonyl, amine and hydroxyl functional groups on the surface of CDs and broad peak in XRD indicates the amorphous nature of the prepared CDs. The overall characterization results suggest the successful synthesis of fluorescent CDs by solvothermal method.

2. Materials and methods

2.1. Materials

*Buchnania lanzan* plant leaves extract was used as the precursor for CDs. Methanol used for extraction was of analytical grade.

2.2. Preparation of leaves extract of *Buchnania lanzan* plant

Fresh leaves of the *Buchnania lanzan* plant were collected and thoroughly washed using tap water and then milli-Q water to exclude dust particles and any unwanted foreign substances. Then, mid ribs of the leaves were removed and leaves were cut into small pieces. Further, exact amounts of leaves were weighed and kept in a beaker filled with specific volume of methanol overnight for cold maceration to take place. The macerated leaves were then crushed in mortar and pestle and filtered to get the final extract.

2.3. Synthesis of CDs

The CDs were synthesized by solvothermal treatment of obtained methanolic extract. Briefly, at first, 10 ml methanolic extract was kept inside a 25 ml Teflon coated stainless steel autoclave and treated for 4 h at 160 °C in an oven. Then, the whole system was cooled at room temperature and the obtained blackish brown solution was centrifuged at 11000 rpm for 30 min (Centrifuge 5804R, Eppendorf) to remove larger particles. The supernatant obtained in the centrifuge tube was further filtered through syringe filter (0.22 µm) to obtain the final CDs solution. The CDs solution was then dried in a vacuum oven to get CDs powder.

2.4. Characterization methods

The UV-Visible absorption spectrum of CDs was obtained using Shimadzu 2450 UV-Vis spectrophotometer. The fluorescence spectra measurement was carried out in SpectraMax i3X, Molecular Devices, using excitation wavelength ranging from 300 nm to 420 nm with an increase of 10 nm. The Fourier-transform infrared (FTIR) spectrum of CDs was recorded using Shimadzu 8400s spectrophotometer. The crystal nature of CDs was analysed by X-ray diffractometer. The zeta potential of CDs was measured using Malvern Zetasizer ver.7.12.

3. Results and discussion
Thus,

The UV-Visible absorption spectrum of prepared CDs (Figure 1A) exhibited two shoulder peaks, one at about 257 nm and other at 356 nm. The first peak is assigned to the $\pi - \pi^*$ transitions of conjugated C=C bonds, while the second shoulder peak is expected due to n - $\pi^*$ transitions of the C=O bonds in CDs [14,15]. CDs solution when kept under UV light (365 nm), it exhibited green colour but in day light it was of brownish yellow colored (Figure 1B). The fluorescence spectra of CDs are presented in Figure 2A. The fluorescence emission spectra showed strong emission with a highest intensity peak at 450 nm under excitation at 350 nm. Further increase in excitation wavelength gradually decreased the peak intensity and a slight shifting in emission maxima is also observed.

![Figure 1](image)

Figure 1. (A) UV-Visible absorption spectrum of prepared CDs. (B) CDs solution in day light (left) and under UV light (365 nm).

Thus, an excitation dependent fluorescence emission behavior is obtained, which is a characteristic feature of CDs and is in accordance with the earlier reports[16]. To identify the surface functional groups of CDs, FTIR spectroscopy was performed. The obtained FTIR spectrum of CDs is presented in Figure 2B. A broad peak centered at 3313 cm$^{-1}$ may be due to O-H and N-H stretching vibrations. Peaks at 2923 cm$^{-1}$ and 2856 cm$^{-1}$ are characteristic peaks of C-H stretching vibrations. The peak seen at 1728 cm$^{-1}$ may be due to C=O stretching. The peak present at 1608 cm$^{-1}$ is because of C=C stretching. The IR peak at 1210 cm$^{-1}$ may be for the C-O stretching and the peak at 1070 cm$^{-1}$ can be of C-N stretching. The overall FTIR spectrum of CDs suggest presence of hydroxyl, carbonyl and amine functional groups on its surface.

![Figure 2](image)

Figure 2. (A) Fluorescence emission spectra of CDs at different excitation wavelengths. (B) FTIR spectrum of CDs.

The XRD pattern of the CDs is shown in Figure 3A. A single broad peak approximately at $2\theta = 19^\circ$ in XRD pattern, suggests the amorphous nature of the prepared CDs. The zeta potential (Figure 3B) of the synthesized CDs was found -10.6 mV. The exhibited negative zeta potential of CDs is in accordance with the FTIR results. The negative zeta potential may be because of hydroxyl and carbonyl functional groups on the surface of
CDs. The overall characterization results suggest the successful synthesis of the fluorescent CDs from Buchania lanzan leaves extract.

![Figure 3. (A) XRD pattern of prepared CDs. (B) Zeta potential of CDs](image)

3. Conclusions

Fluorescent CDs were successfully synthesized by solvothermal treatment of Buchania lanzan leaves extract. The prepared CDs exhibited green fluorescence under UV light and demonstrated excitation dependent emission behavior in the fluorescence spectra. The FTIR spectrum indicated presence of hydroxyl, amine and carbonyl functional groups on the surface of CDs which could serve as an anchoring platform for drugs or other targeting molecules in drug delivery and bioimaging applications. As the CDs were prepared from a renewable (plant) source and good fluorescence property of prepared CDs is obtained, our synthetic scheme can be implemented for bulk production fluorescent CDs and can be utilized in different biomedical applications.

Conflicts of interest: The authors declare no conflict of interest.

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References


