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Development of Fe (III) Sensor System Using Carbon Nanodots Derived from *Plectranthus amboinicus*

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Abstract

Carbon Dots (CDs) are a course of carbon nanomaterials just under 10 nm in dimension endowed with signature optical and electronic properties finding applications in sensors, photocatalysis, biomedical as well as optoelectronics. Single stroke hydrothermal synthesis method seems to have been adopted as the generation of nanocarbon dots from the Indian medicinal plant, Plectranthus amboinicus. Advanced characterisation methods such as UV- Visible absorption spectroscopy, fluorescence spectroscopy, Fourier transform infrared spectroscopy and HR TEM study have been adopted to confirm the structure of carbon nanoparticles. The dependence on the excitation of photoluminescence emission behaviour of CDs have been confirmed using PL spectroscopy. The reaction between the many metal ions with the photoluminescence of CDs are studied and found a striking interaction with Fe (III) ions. The equation from Stern-Volmer is used to study the mechanism of extinction involved in the sensing action of carbon dots and the threshold for recognition is found to be 0.30 µM. The existence of surface functional groups leading to the complexation with Fe (III) ions can primarily be the reason for the observed sensing application. The design and development of eco-friendly sensor systems for Iron metal which is also considered as an essential mineral for human health for its application in biomedical and environmental applications is discussed in this paper.

Keywords: *Biogenic, CDs, Fe Detection, Photoluminescence, Sensors*

1.0 Introduction

Nanomaterials such as carbon, with a size range less than 10 nm and excellent electronic and optical properties, are a recent addition to the fluorescent nanomaterial family. The exceptional advantages such as biocompatibility, water solubility, up-converted photoluminescence, excitation wavelength dependent fluorescence, chemical inertness and robust stability make them an interesting candidate in different technological applications such as optoelectronics, biomedicine, photocatalysis and sensors[1-5]. Current environmental conditions also favours the usage of carbon nanodots owing to the surplus variety of natural sources available for the generation of CDs. The utilisation of the abundant sources due to the syntheis of CDs can help us in putting forward a step towards the environmental conservation[6-8]. Various simple synthesis strategies like as hydrothermal, microwave, pyrolysis techniques have been reported for the development of CDs.

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The occurence of dissimilar functional groups in the carbon nanodots is another unique feature that endows them with excellent solubility and interesting fluorescence properties. Considering its application in various fields also the presence of various functional groups plays a major role. The hydrothermal approach is widely employed for synthesizing of CDs which aids in the modulation of functionalities to be induced into the carbon core[9-12]. Carbon nanodots for the design and development of sensor technology are a vast area in which tremendous research is happening throughout the world. CDs constructed fluorescent sensors for the finding of analytes including various metal ions and some biomolecules such as dopamine, methylene blue etc., have been explored tremendously[13-15].

Since any deviation from the ideal level in the human body can result in serious risks and disorders including Alzheimer's, Parkinson's, hemochromatosis, heart failure, and others, ferric ions (Fe(III)) are of biological importance. Apart from this, Fe(III) is a substantial metal ion whose presence in the consuming water beyond certain limits can lead to health issues in human life. Hence development of a sensor which is environmental friendly as well as economic is of considerable importance. Due to the existence of organic functional groups, CDs can serve as a useful search in favour of sensing of Fe (III) ions[16-20].

This research looked at the synthesis and characterization of CDs using *Plectranthus amboinicus* using one pot hydrothermal method and evaluated its potential in order to detect the Fe (III) metal ions as a fluorescent sensor.

2.0 Materials and Methods

2.1 Materials

Plectranthus amboinicus is obtained from a botanical garden, Thiruvananthapuram, Kerala. Manganous sulphate, Zinc nitrate, magnesium sulphate, sodium chloride, nickel sulphate, ferrous sulphate, copper sulphate pentahydrate, cobaltous sulphate heptahydrate, ferric chloride, mercuric chloride were procured from Sisco research laboratories private limited, India. All throughout preparation and experiments, double-distilled water has been employed.

2.2 Instruments

UV-Visible absorption spectroscopic measurements was executed using Specord 210 plus (make: Analytic Jena) and the fluorescence measurements done using spectrofluorimeter (make: Hitachi F 2700). Fourier transform infrared spectroscopic measurements in ATR mode is obtained from Perkin Elmer Spectrum 1000 at wavelength scan range from 500-4000 cm^{-1}. High resolution TEM images obtained from Joel/JEM 2100 electron microscope.

2.3 Methods

2.3.1 Synthesis of Carbon Dots

Plectranthus amboinicus leaves are thoroughly washed and grinded well in a domestic grinder with little addition of water. The large particles are removed by filtration and the leaf extract is added to a Teflon lined autoclave. The hydrothermal autoclave is held in a hot air oven for six hours with the process permitted to continue at 180 ^{0}C. The resultant solution is filtered through a Whatmann filter paper and centrifuged repeatedly with the addition of ethanol and distilled water to remove the impurities. The solution is vacuum dried overnight at 80 ^{0}C to obtain the brown coloured sticky natured carbon nanodots.

2.3.2 Detection of Fe (III) Ions

The dried CDs concentration was adjusted to 10 mg mL^{-1} concentration. To 3 mL of the CDs, a known concentration (300 µL) of different metal ions solutions (1 mL) has been added separately and incubated for 7 minutes. Then the fluorescence measurements have been carried out at 380 nm excitation for all the samples.

3.0 Results and Discussions

3.1 CDs Characterisation

The UV-Visible absorption spectrum of the as synthesised CDs exhibited two characteristic peaks; one showing the maximum absorption at 271 nm and the other one at 333 nm[21-23]. The appearance of these two peaks corresponds to the n-π* transition of –C=O and π-π* transition of –C=C. Figure 1 depicts the spectrum.

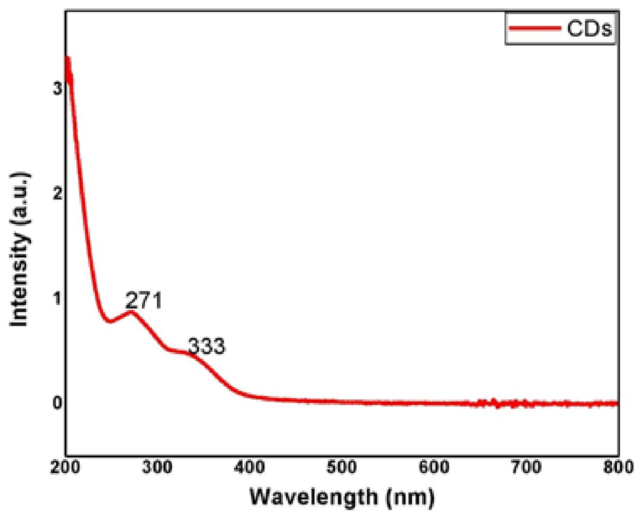

Figure 1. UV-Visible absorption spectrum of CDs derived from *Plectranthus amboinicus.*

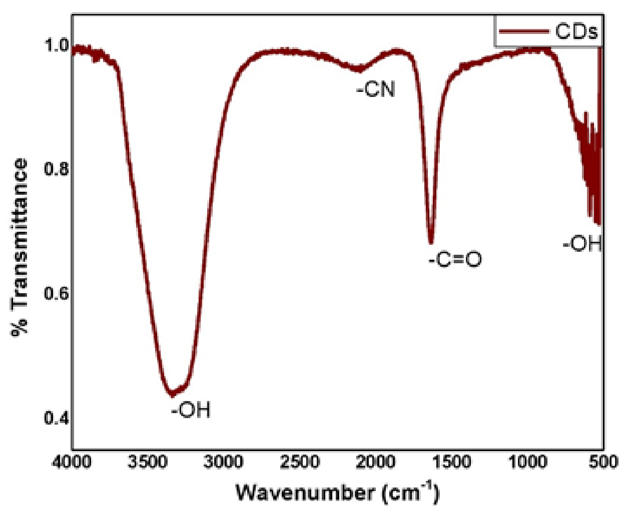

Figure 2. FTIR absorption spectra of CDs.

In Figure 2, the FTIR spectrum obtained for CDs reveal band with maximum at 3341 cm^{-1} resembles to the stretching vibration of –OH. A weak band appeared at about 2100-2000 cm^{-1} belongs to the system's nitrile category. The presence of carbonyl through amide linkage is evidenced by the band originated at 1640 cm^{-1}. From the plane bending vibrations of –OH groups can be identified from the bands emerged at 600-523 cm^{-1} [24-26]. Hence the detailed investigation of the vibrational spectra of CDs reveals the occurrence of -OH, -CO and NH_2 groups in the obtained CDs.

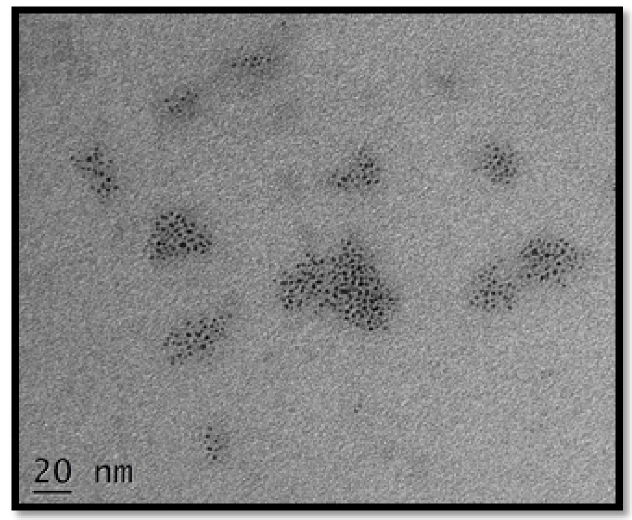

Figure 3. HRTEM image of CDs.

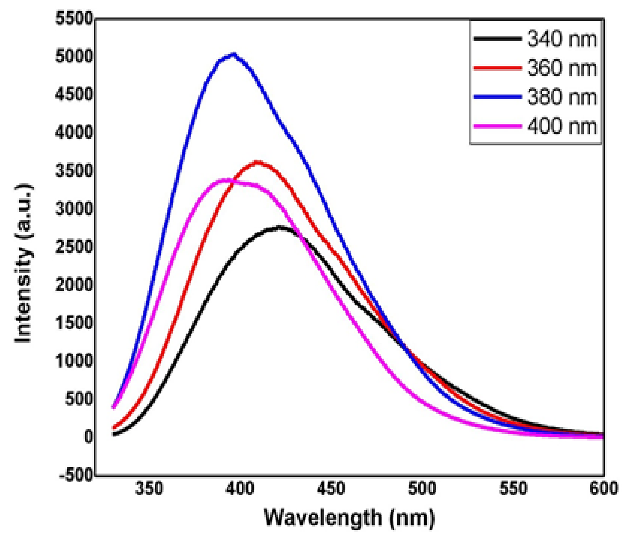

Figure 4. Photoluminescence spectra obtained for CDs excited at different wavelengths.

High resolution TEM pictures have been produced to verify the carbon nanodots' grain size. The particle diameter range of the made CDs is clearly shown in Figure 3 to be within 10 nm. The well-defined spherical morphology with monodispersion of carbon dots with comparatively less agglomeration is noted from the HRTEM images.

A detailed study on the photoluminescence spectra of CDs has been performed and is depicted in Figure 4. The emission peak for the CDs stimulated at 340 nm wavelength was located at 422 nm. The emission intensity likewise rose when the excitation wavelength shifted to the greater side. At an excitation wavelength of 380 nm, the highest intensity of photoluminescence emission was noted. The photoluminescence emission strength started to decline above 380 nm. This suggests that by just changing the excitation wavelength, CDs can exhibit many emission patterns. This discovery can be explained by the optical selection of surface imperfections present in the CDs system[27-30].

3.2 Fe (III) Ions Detection

Since the existence of oxygen-containing functional groups is established by Fourier transform infrared spectroscopy, the influence of dissimilar metal ions on the photoluminescence of CDs has been researched[31]. For the investigation, metal ions including Mn (II), Zn (II), Hg (II), Co (III), Cu (II), Na (I), Fe (III), and Mg (II) were utilized. The concentration of CDs has remained consistent throughout the investigation. A control experiment was conducted without any metal ions. In Figure 5, it is depicted how various metal ions, towards the focus of 300 M, affect the photoluminescence intensity of carbon dots stimulated at 380 nm.

A reduction in the photoluminescence intensity is observed when the inclusion of Fe (III) ions was not seen for any new metal ions which reveals the selectivity of

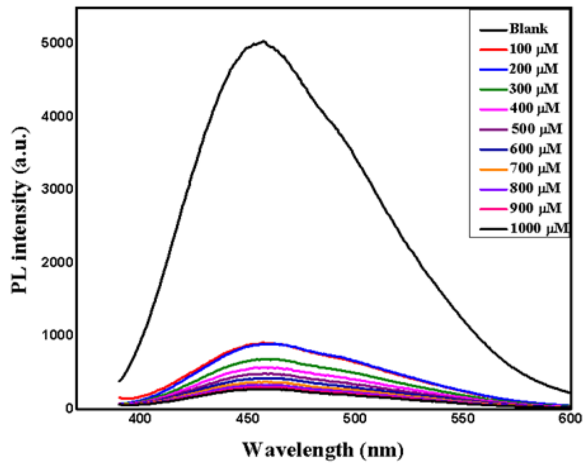

Figure 6. Variation of photoluminescence with the level of Fe (III) ions.

the as synthesised CDs towards Fe (III) ions. The level of Fe (III) ions has been varied from 0-1000 μM and it is found that the intensity of photoluminescence decreases referring to the increase in level of Fe (III) ions as shown in Figure 6.

The Stern-Volmer formula is used to evaluate the quenching phenomenon.

$$\frac{I}{I_0} = 1 + K_{SV}\,[Q] \qquad (1)$$

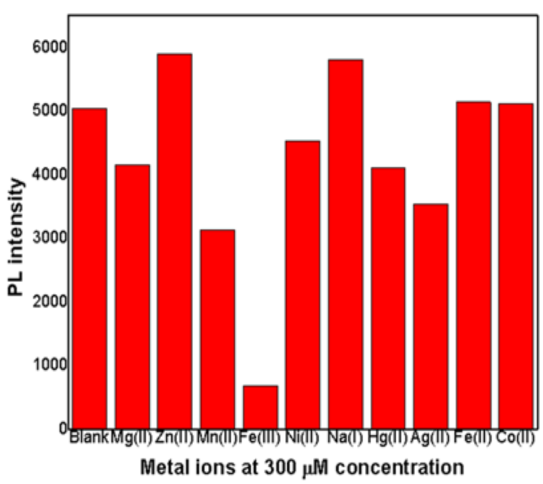

Figure 5. Variation in PL intensity of CDs on interacting with different metal ions.

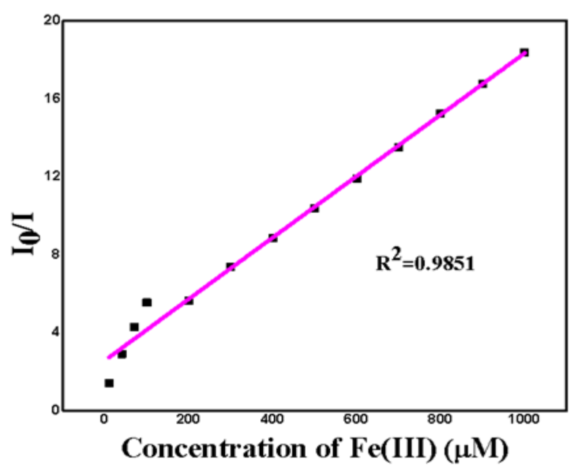

Figure 7. Stern volmer plot ranging from the level of 0-1000 μM.

I_0 is the intensity of the PL emission without a quencher, I is the intensity of the PL emission with a quencher present, K_{sv} is the Stern Volmer constant, and [Q] is the concentration of the quencher[32,33]. With a coefficient of determination of R^2=0.9851, it can be seen that the concentration range of 0-1000 μM exhibits linearity with respect to the Stern-Volmer equation. The static nature of the quenching mechanism and field of action is indicated by this positive slope (Figure 7). Using the Standard Deviation (SD) as a ratio, by the slope of the calibration graph where n=10, three times the SD, the limit of detection was determined. The Fe (III) ion detection sensor system's limit of detection value was 0.38 M, which is less than the World Health Organization's recommended limit of 5.36 μM.

4.0 Conclusion

To conclude, this work explored the synthesis of CDs from the medicinal plant, *Plectranthus amboinicus*. The formation of CDs has been confirmed using UV-Visible absorption, photoluminescence, FTIR and HRTEM analysis. The potential of CDs to sense Fe (III) metal ions are also investigated. It is well understood that the as synthesised CDs show selective and sensitive affinity towards ferric ions. The analysis of Stern-volmer equation reveals the mechanism to be followed in the developed sensor is static quenching with border of exposure of 0.38 μM. This study opens a wide opportunity to design and develop simple metal ion sensors based on the environmental friendly CDs.

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