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Facile Synthesis of Carbon Dots and Photo-induced Detections of Ni Ions

Nasir Javed [1], **Waqas Khalid** [1, 2,] *****, **Javeed Akhtar** [1, 3], **M. Zafar Iqbal** [1]

[1] Materials Lab I, Department of Physics, COMSATS Institute of Information Technology, Park Road, Chak Shahzad, Islamabad, Pakistan
[2] Envioronmental Materials Lab (ENVOMAT), Department of Physics, Air University, Sector E-9, Islamabad, Pakistan.
[3] Polymer and Materials Synthesis Lab (PMS), Department of Chemistry, Mirpur University of Science & Technology(MUST), Mirpur, Azad Jammu & Kashmir, Pakistan
*Corresponding author e-mail address: **waqas.khalid@mail.au.edu.pk**

ABSTRACT

Carbon dots (CDs) possess notable luminescence and hence numerous applications in diverse fields. We propose a commercially viable method to produce CDs. This study reports a facile and cost-effective method to synthesize fluorescent carbon dots with tunable luminescence, using renewable source like sugarcane juice as carbon precursor, which was carbonized in acidic environment by ultrasonication, without any functionalization. Structural and optical properties of the CDs were studied by different spectroscopic techniques. Photoluminescence (PL) spectroscopy revealed that luminescence of CDs depends upon the excitation wavelength, which suggests that it might be due to the presence of surface states. Fourier transform infrared (FTIR) spectroscopy was employed to study the origin of these surface states. These surface states vested the CDs to detect Ni^{2+} ions based on photo-induced electron transfer. Raman spectroscopy suggests that the reported CDs structure is dominant graphitic sp^2.

Keywords: *Carbon dots; Raman spectroscopy; Photoluminescence spectroscopy; Ni ion detection.*

1. INTRODUCTION

It is extremely desirable to have a proper substitute for conventional fluorescent probes, like semiconducting quantum dots, to obviate glitches like photobleaching [1-3], blinking effect [4-6] and especially their toxic nature [7, 8] due to their heavy-metal content [9]. CDs with characteristics like chemical inertness [10, 11], biocompatibility [12-15] and solubility in aqueous media [16, 17], are candidates as most suitable replacements of such conventional quantum dots. Unlike quantum dots, CDs can retain fluorescence even when they lack crystallinity [18]. The surface defect states and hydroxyl content play a prominent role in rendering them fluorescent and water soluble [19]. Excitation dependent fluorescence [20, 21] along with up-conversion [22] properties highlight their superiority over conventional quantum dots. Strongly emissive CDs are finding applications in photovoltaic devices [23, 24], sensing devices [25, 26], *in vitro* [14, 27] and *in vivo* [28, 29] cell imaging and labeling [27].

Metal ion contents along with domestic sewage, industrial effluents and fossil fuel burning are ruining water reservoirs. According to the Department of Economic and Social Affairs, United Nations, number of deaths caused by unsafe water is more than the deaths caused by violence and war. Drinking water quality in Pakistan is poor in general as it is ranked 80 amongst 122 nations in terms of quality of drinking water [30]. Along with other contaminations, A. Waseem et. al. [31] poses a dire picture of abundant presence of heavy metal ions in different lakes in Pakistan. There is a requirement of commercially viable solution to detect the contagious metal ions. Carrying water samples to the centralized laboratories is time consuming. Moreover, the localized concentrations of additives in water may vary during the testing time frame. In this study, CDs can be a possible solution as they can detect Ni^{2+} (a model system) ions via photo-induced electron transfer with in aqueous medium.

CDs have been synthesized using ultrasound energy to breakdown the molecules of diverse types of sugars, present in the precursor: sugarcane juice. In ultrasonic synthesis of CDs, precursor was ultrasonicated in acidic environment. The energy of ultrasonic waves was used for the dehydration/carbonization of sugars [32] and, subsequently, the formation of CDs. We have attempted to analyze the structure as well as surface moieties present in the CDs to get an idea if surface states are the origin of the basic property of photoluminescence, as pointed out in the literature, not infrequently. In fact, the surface states proved vital as we demonstrate the detection of Ni^{2+} ions by CDs via photo-induced electron transfer.

2. EXPERIMENTAL SECTION

Chemicals and measurements. Sulfuric acid (95 – 98 %), which has been used as the principal carbonizing reagent for the synthesis of CDs in our study, was purchased from Merck. Acetone (99.5 %) was purchased from AnalaR. Both chemicals were used as received, without any further purification. Throughout this research, fresh sugarcane juice was used as carbon precursor. Sugarcane juice was filtered before use to remove the insoluble sand and bagasse. Juice was used within 12 h after extraction from sugarcane. X-ray diffraction (XRD) analysis was performed with a PANalytical’s X’Pert PRO X-ray spectrometer, using Cu K-alpha radiation of 1.5418 Å wavelength. Photoluminescence and Raman spectroscopy investigations were carried out, using DongWoo Optron’s Raman and PL measurement system, Model DV420A-OE. UV-Vis absorption spectra were obtained using a Hitachi U-2800 double beam UV-

Vis spectrophotometer. Fourier transform infrared (FTIR) spectroscopy was performed with a Nicolet 6700 spectrometer.

Synthesis of Carbon Dots (CDs). 2.5 mL of 18 M sulfuric acid was added to 5 mL of filtered sugarcane juice. The color of juice quickly changed from greenish to dark brown, implying the formation of carbonaceous material. After ultrasonication for 2 min in ultrasonic bath (Elmasonic E 30 H), excess deionized water was added to it and centrifuged for 15 min (4500 rpm, Gemmy's model: PLC-03). Supernatant emitted bright blue fluorescence when irradiated with 366 nm UV light (CAMAG UV Lamp, Cat. No. 022.9120), which implied the successful synthesis of fluorescent CDs. Precipitates were dispersed in acetone without any sonication and again centrifuged for 15 min. Supernatant emitted yellow fluorescence when irradiated with UV lamp.

Detection of Ni^{2+} ions. Ni^{2+} ions were detected at room temperature in an aqueous solution of CDs. Typically; a stock solution of 10μM of Ni^{2+} ion was prepared in distilled water using salt $NiCl_2$. In a typical run 1ml of CDs were excited at 480 nm and their PL spectra was observed. Then a calculated amount of Ni^{2+} ion solution was added into the 1ml CDs and left at room temperature for 5 min for the chemical reaction to take place. Ionic solution containing CDs were again excited at 480 nm and PL spectrum was recorded. This process was repeated for different calculated concentration of ionic solution.

3. RESULTS SECTION

Figure 1 represents the schematic illustration of synthesis of CDs from the renewable source of sugarcane juice. Scheme indicates the formation of CDs via ultrasonication and collection of different fragments via centrifugation.

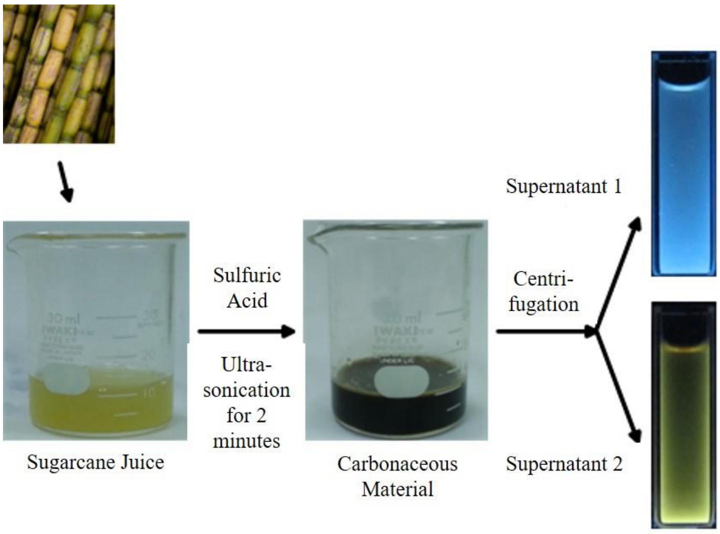

Figure 1. Schematic illustration of carbonization of sugar cane juice and extraction of two fractions of CDs, irradiated with 366 nm UV light.

The X-ray diffraction (Figure 2a) pattern shows a broad peak centered at 23.51° (2θ), which corresponds to inter-planar spacing of 3.78 Å. This spacing is slightly greater than the lattice spacing (3.4 Å) of (002) planes of bulk graphite [33]. No other feature of graphite was observed, which indicates that CDs are poorly crystallized or amorphous. It seems that CDs are formed by the loose stacking of graphene layers. The broadness of the peak is a sign of non-uniform inter-planar spacing, which may be alluded to non-uniformity in the size of particles comprising the sample.

The broad absorption band in FTIR (Figure 2b) of CDs centered at 3196 cm^{-1} identifies the presence of –OH group on the surface of CDs. Presence of this group is responsible for the hydrophilicity of CDs. Absorption peaks at 2922 cm^{-1} and 2854 cm^{-1} correspond to asymmetric and symmetric stretching of alkyl C-H bonds, respectively. Presence of C=C double bond was also represented by the transmittance valley at 1614 cm^{-1}. Stretching vibration of carbonyl C=O corresponds to the absorption peak at 1695 cm^{-1} [34]. Presence of C-O bond was detected by the absorption band at 1026 cm^{-1}, which corresponds to the stretching vibration of this bond [35].

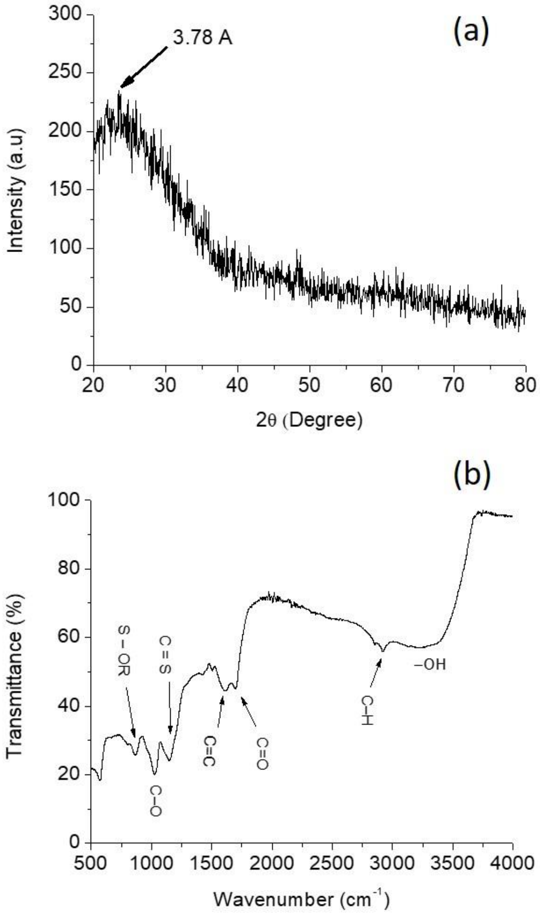

Figure 2. (a) Typical X-ray diffraction pattern of CDs, (b) FTIR spectrum indicating different functional groups on CDs

Raman spectrum of CDs, shown in Figure 3, was recorded to check the nature of CDs, i.e., if they have sp^2 or sp^3 bonding configuration. The spectrum showed a broad peak at 1370 cm^{-1} and a sharp peak at 1614 cm^{-1}. These peaks were assigned to D-band and G-band of graphitic and/or amorphous carbon, respectively. The presence of D-band suggests the occurrence of dangling bonds in graphitic or amorphous carbon and G-band implies the vibration of sp^2 carbon bonds in graphitic structure [38]. Presence of both bands suggests that either the CDs are amorphous or the core of CDs is graphitic and plenty of dangling bonds may exist on their surfaces, which is normal for nano-sized particles [38]. Relative intensity of these two bands is less than one (I_D/I_G = 0.71), which indicates that CDs are dominantly graphitic (sp^2) in nature [19, 38]. These Raman results strengthen our suggested interpretation based on XRD and FTIR results.

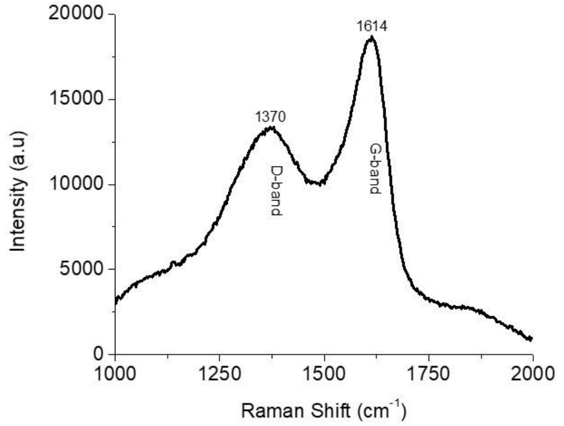

Figure 3. RAMAN spectrum of CDs having a dominant graphitic structure

For the optical characterizations, initially UV-Vis absorption spectra of blue and yellow fluorescent CDs were recorded (Figure 4a). Absorption spectrum of dilute aqueous solution of blue luminescent CDs (solid line) shows a narrow absorption peak at 308 nm (4.03 eV). Steps in UV-Vis absorption spectra at 370 nm are due to the change of lamp. Dashed curve in Figure 4a show the UV-Vis absorption spectrum of yellow luminescent CDs suspended in acetone. The spectrum shows an absorption peak at 337 nm (3.68 eV). The spectrum is relatively broader than that of blue luminescent CDs. It was observed that absorption of yellow luminescent CDs in visible region is higher as compared with blue luminescent CDs. Absorption band in ultraviolet region, which was observed in blue and yellow luminescent CDs is attributed to excitation of π bond in organic compounds [19, 34, 39]. High absorption intensity in visible region can be due to Mie scattering caused by nanoparticles [19], in addition to the contribution of the defect states.

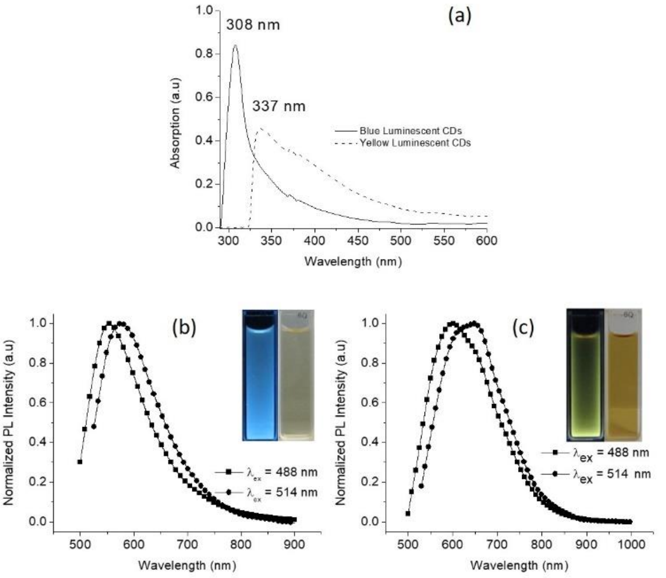

Figure 4. (a) UV-Vis spectrum of blue (solid line) and yellow (dashed line) CDs, (b) PL of blue CDs, excited at 488 nm and 514 nm, inset indicates the excitation with UV lamp at 366 nm, (c) PL of yellow CDs, excited at 488 nm and 514 nm, inset indicates the excitation with UV lamp at 366 nm.

Photoluminescence (PL) emission spectra of both blue and yellow CDs were taken using two different excitation wavelengths of the Ar-ion laser, i.e. 488 nm and 514 nm. The PL emission spectra of blue luminescent CDs for the two excitation wavelengths are shown in Figure 4b and 4c, indicating excitation dependence of emission of CDs. Peak of PL emission spectrum moves towards longer wavelength (553 nm to 576 nm) as the wavelength of excitation laser is increased (from 488 to 514 nm). Inset shows the pictures of the aqueous solution of these CDs, excited with UV light of wavelength 366 nm (left) and in ordinary room light (right). Surface states, associated with the presence of chemical functional groups (as indicated by the FTIR spectra) are seemingly the reasons of strong luminescence in CDs.

It was observed that luminescence of these CDs was stable. CDs were stored at room temperature and same luminescence was observed after as long as eight months since their synthesis. No shift in peak position or degradation in luminescence intensity was observed after repeating the photoluminescence measurement. The synthesis of CDs was repeated several times with the same method, to confirm the reproducibility of results. No appreciable change was observed in UV-Vis absorption and photoluminescence emission properties.

Detection of Ni^{2+} ions was done via PL spectroscopy (Figure 5). CDs were first excited at 480 nm and their PL spectrum was recorded. Then a typical Ni^{2+} concentration was added to CDs dispersion. CDs were again excited at 480 nm and their PL spectrum in presence of Ni^{2+} ion was recorded. The PL spectra for different calculated concentrations of Ni^{2+} ions were recorded.

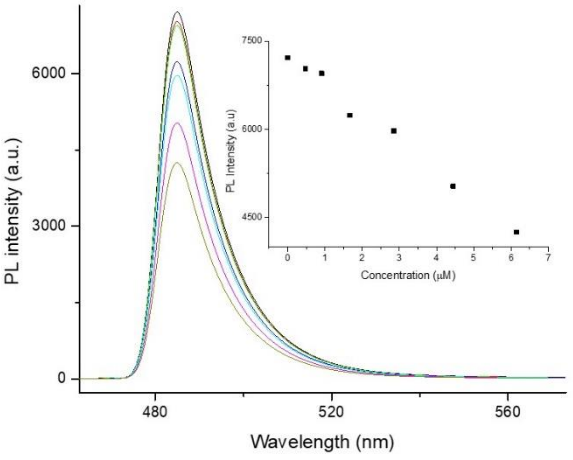

Figure 5. Stepwise quenching in PL with increasing concentration of Ni^{2+} ions, inset indicates almost linear decrease in PL signal of CDs with increasing Ni^{2+} concentration.

A fluorescence response of CDs in the presence of Ni^{2+} ions is illustrated in the inset of Figure 5. The PL signal quenches as the concentration of Ni^{2+} increases, may be because of photo induced electron transfer. Many defect states available at the surface of CDs can cause the trapping states. The long lived excited state originates as electron gets trapped into the defect state and the case may arise during the non-radiative decay, where Ni^{2+} might be neutralized by transfer of electron from CDs, given the circumstances are thermodynamically favorable. As the presence of Ni^{2+} ion increases in the solution the radiative decay within CDs seems passive, and more and more electrons seem to be used up to defuse Ni^{2+} ions. Around 40% fluorescence of CDs is quenched with an addition of 6 μM ionic solution which makes CDs very sensitive probes for Ni^{2+} ions in an ionic solution.

4. CONCLUSIONS

Fluorescent CDs have been successfully synthesized in one step by ultrasonication of sugarcane juice in the presence of sulfuric acid, without any surface functionalization. During the synthesis, hydroxyl, carboxyl and other organic functional groups attach to the surface of CDs, as suggested by FTIR analysis. The presence of D-band and G-band in Raman spectrum suggests a dominating sp^2 (graphene like) structure and XRD suggests that the graphene layers loaded with above-mentioned functional groups are loosely stacked together to form the carbon dots. Energy states on the surface of CDs caused by organic functional groups may be the origin of excitation-dependent fluorescence. The surface states of CDs enabled them to be sensitive towards Ni^{2+} ions via photo-induced electron transfer.

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6. ACKNOWLEDGEMENTS

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