SYNTHESIS AND CHARACTERIZATION OF FLUORESCENT CARBON QUANTUM DOTS AND THEIR MULTIFUNCTIONAL APPLICATIONS

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By

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The current thesis work described the synthesis of fluorescent carbon quantum dots (CQDs). The CQDs were synthesized by natural organic precursors by using simple one-pot hydrothermal method. CQDs have excellent properties such as strong fluorescence emission, economical, high quantum yield (QY), good water solubility, excitation-dependent emission, easy surface functionalization, and low cytotoxicity. To characterize fluorescent CQDs, several instrumental techniques such as Transmission Electron Microscopy (TEM), Selected Area Electron Diffraction Pattern (SAED), X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR) Spectroscopy, Energy-Dispersive X-Ray Spectroscopy (EDAX), X-Ray Photoelectron Spectroscopy (XPS), UV-visible Spectroscopy and Fluorescence Spectroscopy were utilized. The as-synthesized CQDs were applied as peroxidase-mimetic enzyme activity, for the detection of hydrogen peroxide (H_2O_2), ascorbic acid (AA), Fe (III), cellular imaging and to fabricate schottky barrier diodes. In addition to this, the potential feasibility of the proposed sensing system was further investigated in real natural samples.

Chapter 1 The present chapter deals with the extensive literature survey associated with efficient and economically viable green route for the synthesis of fluorescent CQDs. Different types of nanomaterials were described in this chapter along with their various synthesis approaches. Current chapter also examines an overview and history of CQDs. The properties and applications of fluorescent CQDs along with their objectives have also been discussed in the present chapter.

Chapter 2 This chapter provides details about the materials and the methods utilized in the current thesis work. The current chapter also offered the list of chemicals which have been utilized all over the experiments. The detail about the synthetic methods of fluorescent CQDs

and the experimental processes used for various applications like detection of ascorbic acid (AA), hydrogen peroxide, Fe (III), Tyrosine and fabrication of schottky barrier diodes, have also been covered in this chapter.

Chapter 3 In the present study, an eco-friendly and zero-cost approach has been established for the synthesis of CQDs by one-pot hydrothermal treatment of leaf extracts of Neem (*Azadirachta indica*). To determine the size and morphology of N-CQDs, high resolution TEM studies was carried out which showed the spherical shape of N-CQDs. The corresponding histogram established that the average size of N-CQDs was 3.2 nm distributed in the range from 1 to 5.5 nm. The SAED pattern revealed the amorphous nature of N-CQDs which was further supported by P-XRD analysis with a broad peak at $2\theta = 24.5°$. The EDAX convoluted the presence of C (81.56 %), O (9.82 %) and N (7.15 %) elements present in N-CQDs. FT-IR spectroscopy confirmed the presence of different functional groups such as -OH, $-NH_2$, and C=O on the surface of N-CQDs. The Zeta potential of N-CQDs was -4.78 mV, revealing the negative charge on the N-CQDs surface. To determine the elemental state, bonding present and composition, XPS analyses were performed which revealed the presence of C 1s (285.70 eV), N 1s (400.59 eV) and O 1s (533.22 eV). The UV–Vis absorption spectra of N-CQDs showed two peak at 276 nm and 340 nm which attributed to the π–π^* and n–π^* transition respectively. The QY of fluorescent N-CQDs was calculated to be 27.2 % with respect to reference quinine sulfate. The effect of pH on the fluorescence emission of N-CQDs was also investigated and was observed that it was stable in a wide pH range from 5 to 9. In addition to this, we have investigated the effect of ionic salt on the fluorescence emission intensity of N-CQDs and observed no considerable decrease in the fluorescence emission intensity, revealing stability in high ionic salt conditions [KCl solution (0.5 to 5

M)]. The as-synthesis N-CQDs exhibited peroxidase-mimetic enzyme activity and were involved in the oxidation of colorless TMB into blue color oxidized TMB in the presence of H_2O_2. The detection system showed good linearity from 0.1 to 0.5 with limit of detection (LOD) 0.035 mmol/L. The blue color of ox-TMB offered an excellent platform for the sensing of reductant molecules. As a result, the blue colors of oxidized TMB (ox-TMB) were selectively reduced in native TMB with ascorbic acid (AA) without interfering with other reducing agents. The LOD was calculated to be to 1.773 μM with a linear range of 5-40 μM. The practicability feasibility of the proposed sensing was further investigated in the real sample such as common fresh fruits.

Chapter 4 In this chapter, a facile, green and eco-friendly approach has been utilized for the synthesis of green-blue carbon dots (GB-CDs) by using one-step hydrothermal treatment of *Artocarpus lakoocha* seeds. The TEM image showed the spherical morphology of GB-CDs ranges from of 2.5 to 8.5 nm with an average size of 4.9 nm. The SAED patterns examined crystal defects and exposed the amorphous nature of GB-CDs. The XRD study further confirmed the amorphous nature with a broad peak at $2\theta = 23.5°$. The existences of different functional groups such as OH, $-NH_2$, and -C=O on the surface of GB-CDs were inspected using FT-IR spectrum. The zeta potential of the GB-CDs was obtained to be -20.26 mV revealed negative charge on GB-CDs. Further, stability of GB-CDs was performed in different pH and highly ionic salt concentrations. The as-synthesized GB-CDs exhibited high fluorescent QY up to 38.5%. GB-CDs was effectively utilized for the selective and sensitive detection of Fe^{3+} with a LOD 0.6 μM and linearity from 2 to 6 μM. The quenching of Fe^{3+} was due to a combination of inner filter effect (IFE) and dynamic quenching. The dynamic quenching was further confirmed by a fluorescence life-time measurement experiment. The detection of Fe^{3+} was further explored in the river water and human blood serum. In addition to this, MTT assay was performed on SH-SY5Y neuroblastoma cells which showed negligible cytotoxicity and high cell viability that revealed their application in cellular imaging.

Chapter 5 In this paper, a simple and straightforward approach has been deliberated to synthesize fluorescent green carbon quantum dots (G-CQDs) by using the latex of ficus benghalensis as a carbon source and polyethyleneimine as a nitrogen source. The TEM confirmed the spherical morphology and the average size histogram reveals the average size of 3.7 nm distributed from 1 to 6 nm. The XRD pattern showed a broadband at $2\theta = 24.7°$ revealing the amorphous nature. The FT- IR spectrum confirmed the existence of different functional groups on the surface of G-CQDs. The binding and the elemental composition were explored by XPS study. Interestingly, as-synthesized CQDs exhibited green fluorescence with QY 41.2%. The G-CQDs were applied as a selective and sensitive detection of Tyrosine (Tyr) with a LOD 0.13 μM with linearity from 2 to 6 μM. Further, to explain the quenching mechanism, the fluorescence lifetime experiment was performed which confirmed static quenching. The detection of Tyr was also performed in milk sample. In addition to this, the synthesized G-CQDs were successfully applied to fabricate a Schottky barrier diode on Indium doped tin oxide (ITO) substrate.

Following the widespread literature survey related to the synthesis of fluorescent carbon quantum dots from different organic precursors and completion of the current thesis work, the given below suggestion could be helpful for the fabrication of fluorescent CQDs and their applications in future.

- Several techniques have been utilized for the efficient preparation and optimization of CQDs. However, one step hydrothermal treatment is superior for the preparation of CQDs in contrast to other synthesis techniques. Yet in near future there are some avenue to investigate the synthesis and optimization of CQDs by different synthesis methods.
- Although different methods have been used for CQDs synthesis, however there is no report on atom-precise and well-defined structures which is an imperative to determine the relationships between structure and properties, specific management of properties, and investigation of new methods and applications.
- In most of the research paper, it has not been reported that why the doped and co-doped CQDs have high fluorescence QY as compared to the un-doped CQDs. Therefore, in future it is possible to evidently understand the intrinsic fluorescence mechanism in doped and co-doped CQDs and should expected additional theoretical and experimental works and combinations.
- Moreover, most of the doped and co-doped CQDs emit blue fluorescence. Therefore, it is challenging task for researcher to synthesize multi-color emission CQDs and utilized in different applications in future.

- ❖ Furthermore, it has been found that CQDs can be proficiently exploited in an extensive range of applications including fluorescent ink, drug delivery, LED’s, detection of pesticides, photocatalysis, temperature probe fungicides and solar cells.