SYNTHESIS OF CARBON BASED FLUORESCENT NANOMATERIALS AND THEIR APPLICATIONS

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The importunity of this thesis is to develop various types of carbon-based fluorescent nanomaterials for detection of hazardous compounds using natural and organic carbon precursors. The CQDs have been synthesized by one-pot hydrothermal method due to its simplicity, rapidity, controlled reaction conditions, and cost-effectiveness. Several modern techniques were used for characterization of the CQDs, including Fourier Transform Infrared (FTIR) Spectroscopy, UV-visible Spectroscopy, Fluorescence Spectroscopy, Transmission Electron Microscopy (TEM), Energy-Dispersive X-Ray Spectroscopy (EDAX), Selected Area Electron Diffraction Pattern (SAED), and X-Ray Photoelectron Spectroscopy (XPS). Moreover, these CQDs have been implemented in sensing applications for ascorbic acid, hydrogen peroxide picric acid, and chlorpyrifos detection. As well as this, the potential feasibility of the proposed sensing system was successfully debated on the basis of a real-life natural sample analysis.

Chapter 1 cover the basics of nanotechnology, its origins in brief, and the different types of nanomaterials. In addition to this, the section also contains a brief history of previous and ongoing research on the synthesis of CQDs and their applications. The goals and scope of the present investigation have been outlined at the end of this chapter.

Chapter 2 In this section, the experimental details, including the materials and instruments that have been used to fully characterize the carbon quantum dots, are discussed. In this chapter, the preparation of standard solutions and various calculations are also covered, such as quantum yields, quenching constants, and limit detection of detections.

Chapter 3 summarized the fabrication of fluorescent carbon quantum dots via facile one-step hydrothermal method of mustard seeds (M-CQDs). It showed excellent optical property

with fluorescent quantum yield 4.6 %. The structural and compositional analysis of M-CQDs were performed by X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), and x-ray photoelectron spectroscopy (XPS) and FT-IR spectroscopy. Furthermore, the optical properties of synthesised M-CQDs were characterised by UV-visible, fluorescence and fluorescence lifetime spectroscopy. The as-prepared M-CQDs exhibited peroxidase-like mimetic activity and catalyzed the oxidation of chromogenic substrate 3,3',5,5'-tetramethylbenzidine (TMB) in the presence of H_2O_2 to produce a blue color reaction mixture with the prominent peak at 652 nm. Furthermore, the peroxidase-like activity performance of M-CQDs followed the steady-state kinetics behavior and exhibited similar catalytic activity as that of natural enzyme Horseradish peroxidase (HRP). In addition to this, the double reciprocal plot showed a parallel line which suggested the occurrence of Ping-Pong type of mechanism. The H_2O_2 dependent oxidation of TMB was helpful for the colorimetric detection of H_2O_2 in the linear range of 0.02 to 0.20 mM with the limit of detection (LOD) of 0.015 mM. Interestingly, the oxidized TMB was further reduced to native TMB by the reducing agent ascorbic acid. Hence M-CQDs showed its potential towards the selective and sensitive detection of ascorbic acid in the linear range of 10 to 70 μM having a correlation coefficient of 0.998 with LOD of 3.26 μM. The practical feasibility of the proposed detection method of AA was also investigated in common fresh fruits.

Chapter 4 the present study aims the development of hazardous explosive picric acid sensor based on the NS-CQDs. In this work, we utilize a one-pot hydrothermal technique for the synthesis of nitrogen/sulfur-co-doped fluorescent carbon quantum dots (NS-CQDs) from citric acid (CA) and thiosemicarbazide (TSC) at 180 ^{o}C for 5 h. The obtained NS-CQDs exhibited strong blue emission under UV light. The Commission internationale de l'eclairage (CIE) coordinates originated at (0.15, 0.07), which confirmed the blue fluorescence of the synthesized NS-CQDs. The as-prepared NS-CQDs shown the excitation-dependent tuned emission in the range of 240–400 nm with the high fluorescence QY 37.8 %. Interestingly, the prepared NS-CQDs were successfully used as a selective nanoprobe for the monitoring of environmentally hazardous explosive picric acid (PA) in different nitro- and non-nitro-aromatic derivatives of PA. Moreover, the synthesized NS-CQDs served as a sensitive nano-probe for the detection of PA with high selectivity and sensitivity along with the limit of detection (LOD) 0.22 mM in the obtained linear range of 0–3 μM of PA concentrations. The mechanism of the NS-CQDs was also explored, and was posited to occur via the fluorescence resonance electron transfer (FRET) process and non-fluorescent complex formation. Importantly, this system possesses excellent biocompatibility and low cytotoxicity in HeLa cervical cancer cells; hence, it can potentially be used for PA detection in analytical, environmental, and pathological applications. Furthermore, the practical applicability of the proposed sensing system to pond water demonstrated the feasibility of our system along with good recovery.

Chapter 5 reports the hydrothermal method for the fabrication of fluorescent carbon quantum dots (J-CQDs) from Jatropha fruit at 180^0C for 5 h. Now a days, green route are significantly favoured for the synthesis of CQDs, which develop the use of natural renewable carbon sources. The use of green sources has several advantages due to zero cost, non-toxicity, environmental friendliness, and easy availability. In this study, we have synthesized J-CQDs for the first time. The as-synthesized J-CQDs exhibited bright blue fluorescence emission with a high quantum yield of 13.7 %. Furthermore, the synthesized fluorescent J-CQDs have been used as a fluorometric sensor for the detection of pesticides. The sensing of pesticides is based on the irreversible catalytic inhibition of acetylcholinesterase (AChE) enzyme with a controlled fluorescence quenching process. The thiocholine was mainly triggered by the decomposition of DTNB to form yellow-colored TNBA. Further, TNBA gradually quenched the fluorescence emission spectra of added J-CQDs via electron transfer process. The catalytic activity of AChE was inhibited in the presence of OPs, leading to the recovery of the fluorescence signal. Thus, a sensitive and selective nanoprobe was designed for the sensing of OPs (chlorpyrifos) along with a detection limit 2.7 ng/mL. Apart from this, the proposed sensing method has been successfully applied for pesticide detection in environmental and agricultural samples with acceptable recovery. Thus, the delivered result suggests that our probe is simple in design, having a short reaction time, and could be proficiently used in further analytical and environmental applications in the future. The proposed sensing system was successfully applied on natural samples with good recovery efficiency. Therefore, the suggested method is scalable for analytical applications in food security and environmental monitoring fields and will provide favorable solutions for investigating of pesticide residues.

The thesis work has primarily focused on synthesizing different types of fluorescent CQDs using natural and chemical precursors. In order to continue the work, the following suggestions might be helpful when manufacturing CQDs and applying them in the future.

- ❖ There has been a great deal of research on the actual preparation and optimization of CQDs. As a comparison to other synthesis methods, the hydrothermal method is the most common method used for the synthesis of these CQDs. However, in the near future, more avenues will be explored for preparing and optimizing these CQDs using different synthesis protocols.
- ❖ Although CQDs have been prepared by numerous facile synthetic methods, atom-precise and well-defined structures haven't been reported yet, which is critical for studying the relationship between structure and properties, precisely controlling properties, and exploring new application areas.
- ❖ Doped and co-doped CQDs exhibit enhanced fluorescence QY with respect to normal CQDs, but the reasons for this enhancement are not fully understood in most research studies. Thus, future studies will be able to clarify the intrinsic mechanism of photoluminescence in doped and co-doped CQDs. As a result, theoretical and experimental works and combinations are to be expected.
- ❖ In addition, many of the synthesized fluorescent CQDs can be used as optical sensors and could also be used for various other applications in the future. Furthermore, fluorescent CQDs are suitable for use in biological applications such as drug delivery, bio-imaging and biomedicine.

- Moreover, it has been established that the CQDs can be efficiently exploited in wide range of applications counting LED's, solar cells, fluorescent ink, energy storage devices, and detection of pesticides, and photo-catalysis. Consequently, the findings are likely to contribute substantially to the future of fluorescent CQDs as emerging materials.