Preface

The present thesis represents the development of different type of carbon based nanoprobe synthesized by the chemical and biological precursors for the detection of metal ions and biosensor. Recently, carbon quantum dots (CQDs) are a demanding class of advanced fluorescent nanomaterials compared to other metal based semiconductor quantum dots in aspects of sturdy fluorescence emission, high quantum yield, economical, high water solubility, easy functionalization, and low-cytotoxicity. These materials are regarding as zero dimensional (0D) materials. They have size in the range of 1 and 10 nm and are also recognized by different names including carbon dots (CDs) and carbon nanoparticles (CNPs). Due to the large surface and high surface energy, it could be used in the broad applications including catalysis, bioimaging, optronic devices, and sensing applications. Various efforts have been made in the synthesis process to improve the functionality and optical properties of CQDs using different techniques including laser ablation, arc discharge, chemical oxidation, electrochemical oxidation, hydrothermal carbonization, and microwave irradiation. Among them, laser ablation and arc discharge need sophisticated and expensive instruments, and chemical oxidation and electrochemical oxidation require very strong acids. Microwave irradiation provides an easy path way to synthesize CQDs within a few minutes; however, it is limited by its uncontrollable reaction conditions. At present, the hydrothermal route is frequently preferred due to its simplicity, rapidity, controlled reaction conditions, and cost-effectiveness. There are many organic compounds, such as ascorbic acid, tartaric acid, citric acid, glycol, glucose, sucrose, and glycerol that have been used for the synthesis of CQDs. For surface passivation, many organic polymeric moieties, such as polyethyleneimine, polyethylene glycol, and 4,7,10-trioxa-1,13-tridecanediamine, and so on have been

frequently used. In addition CQDs could also be synthesized via natural organic precursors. To date, numerous studies utilizing natural green sources, such as soybean, pomelo peel orange juice, green grass, milk, potato, plant leaves, soy milk, cocoon silk, and so on for the synthesis of CQDs have been reported. Though, the key challenge is still to develop CQDs with high quantum yields (QY).

Chapter 1 covers the basics of nanotechnology and its origin in brief, different type of nanomaterials. In addition to this, a brief historical review of ongoing and the past research on synthesis of CQDs and their applications has been incorporated in this section. The scope and objectives of the present investigation have been highlighted at the end of this chapter.

Chapter 2 describes of the experimental details including required materials and instrumentation which have been used thoroughly to characterize the carbon quantum dots. The current chapter also covers the details of various application such as bioimaging, cell cytotoxicity and detection of GSH and metal ions.

Chapter 3 encompasses the synthesis of fluorescent nitrogen rich carbon quantum dots (N–CQDs) by using glycine and polyethyleneimine precursors through the hydrothermal approach. In this study, glycine is used as a carbon and nitrogen precursors and polyethyleneimine is used as a nitrogen doping as well as surface passivating agent. The synthesized N–CQDs exhibited the strong blue fluorescence at the excitation wavelength of 365 nm under UV light along with CIE co-ordinate index (0.15, 0.14). Moreover, the as-prepared N-CQDs demonstrated very high QY up to 57% using quinine sulfate as a

reference. By using these N–CQDs, very selective and sensitive approach is developed for the detection of Co^{2+} via quenching mechanism. Inspired by these outstanding properties, the as-prepared N-CQDs were also successfully employed for the practical application toward monitoring the trace level of Co^{2+} in a vitamin B–12 sample.

Chapter 4 the present study aims the development of glutathione (GSH) sensor based on the N,S–doped CQDs and MnO_2 nanocomposites (N,S–CQD–MnO_2). The N,S–CQDs were synthesized via hydrothermal treatment of tartaric acid and taurine precursors. The synthesized N,S–CQDs exhibited strong blue emission at 365 nm excitation. The measured QY was high up to 47.4%. MnO_2 nanosheet possess broad absorption spectrum between 250 and 600 nm which can act as an efficient broad spectrum quencher. In this study, we have assembled a N,S–CQD–MnO_2 nanocomposite by simple ultrasonication method. Introduction of MnO_2 nanosheets quenches the fluorescence emission of N,S–CQDs by the phenomenon of fluorescence resonance energy transfer and strong electrostatic interactions between them. Furthermore, MTT assay also confirmed that the as-prepared N,S–CQD–MnO_2 based nanoprobe show very low cytotoxicity and good biocompatibility. The calculated detection limit was found to be 0.012 μM in a GSH concentration having a linear range of 0.1–0.7 μM. The fluorescence can reappear after the addition of GSH into the nano-composite solution because it triggers the decomposition of MnO_2 nanosheet into Mn^{2+}, which leads to the elimination of fluorescence resonance energy transfer. In

addition, the developed nano-composite based material could act as an efficient nanoprobe for *in vitro* inspecting GSH in living cells and human blood serum.

Chapter 5 addresses the green synthetic approach for the synthesis of water-soluble fluorescent CQDs. Now a days, green route are considerably preferred 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, CQDs were synthesized through the simple one-step hydrothermal treatment using Tamarindus indica leaves for the first time. This methodology involves zero cost, short reaction time, and double-distilled water as the reaction solvent. There is no need for additional surface passivating reagents since the T. Indica leaves serve as both the carbon precursor and surface passivating agent. The prepared CQDs showed an excitation-dependent behavior in the range from 260 to 400 nm with a high QY of approximately 46.6%. Further, the prepared CQDs serve as a very sensitive nanoprobe for the turn-off sensing of Hg^{2+} with a minimum LOD as low as 6 nM in the dynamic range from 0 to 0.1 mM. The attractiveness of the present sensing system is that it further acts as a turn-on sensor for GSH detection with good selectivity. The feasibility of the present sensing system is also examined using pond water samples for the detection of Hg^{2+}. Thus, the present sensing system is reliable for sensing and several another analytical applications.

Chapter 6 illustrates the green synthetic approach for the development of water soluble CQDs. In this study CQDs were synthesized by facile single-

step hydrothermal treatment of latexes of *E. milii* plant for the first time. The as-prepared CQDs exhibited blue color emission under the 365 nm excitation including high QY up to 39.2 %. The CQDs resisted the high salt strength condition and long-time photostability. Moreover, the as-prepared CQDs served as an intrinsic peroxidase mimetic activity to catalyze the chromogenic substrate 3,3',5,5'-tetramethylbenzidine (TMB) in association with H_2O_2 which resulted into a blue color reaction along with a characteristics absorbance peak at 652 nm. Further, the produced blue color system can act as a turn-off probe for the sensing of GSH by changing the color of the reaction system blue to transparent which can be seen easily. The selectivity experiment in presence of various amino acids and several other interfering agents confirmed that our designed TMB based oxidation probe could work as an efficient probe for the GSH detection. The measured LOD was calculated to be 5.3 nM in a linear range 0.02 to 0.1 μM of GSH concentration which showed superiority under the optimal condition as compared to another probe. To demonstrate the practical feasibility for the GSH detection, the present system was successfully applied on human blood serums with good recovery.