

List of Figures

Figure No.	Title	Page No.
Figure 1.1	Structure of various allotropes and nanostructure of carbon	5
Figure 1.2	Illustration of FRET process through Jablonski diagram	25
Figure 2.1	Schematic representation of principle of Transmission electron microscopy (TEM)	47
Figure 2.2	Photograph of Transmission electron microscopy (TEM)	48
Figure 2.3	X-rays diffraction by crystal plane (Bragg's law)	49
Figure 2.4	Schematic representation of principle of X-Ray diffraction (XRD)	51
Figure 2.5	Photograph of X-Ray diffraction spectroscopy (XRD)	51
Figure 2.6	Schematic representation of working of Fourier transform infrared (FTIR) spectrophotometer and its photograph	53
Figure 2.7	Working principle of X-ray photoelectron spectroscopy (XPS)	54
Figure 2.8	Typical photograph of XPS instrument	55
Figure 2.9	Working principle of Zetasizer and its photograph	56
Figure 2.10	Schematic representation of possible electronic transitions in UV-visible spectroscopy	58
Figure 2.11	Schematic diagram of UV-visible spectrophotometer	59
Figure 2.12	Typical photograph of UV-visible spectrophotometer	59
Figure 2.13	Schematic representation of working principle of fluorescence spectrophotometer	61
Figure 2.14	Photograph of fluorescence spectrophotometer	61
Figure 3.1	(a) TEM micrograph of N-CQDs whereas inset shows the SAED micrographs of N-CQDs, (b) particle size histogram, (c) XRD spectrum of N-CQDs at scan rate 5°/min in a range 10–70°, (d) FTIR spectrum of the as-prepared N-CQDs in a range 500–4000 cm ⁻¹ .	68
Figure 3.2	EDAX analysis of the as-prepared N-CQDs composed of C, O and N, inset shows the elemental composition.	69
Figure 3.3	Correspond to the (a) Wide scan spectrum, (b) C 1s spectra, (c) O 1s spectra, (d) N 1s spectra of the N-CQDs.	70

Figure 3.4	(a) UV-visible spectrum (black) and FL emission intensity (blue) at the excitation wavelength of 360 nm of N-CQDs, (b) CIE co-ordinates for the blue FL emission of N-CQDs, (c) represents the FL emission intensity at the different excitation wavelength (280–400 nm), (d) showing the stability under high ionic strength after the addition of different NaCl concentration (0–100 mM)	72
Figure 3.5	Stability of N–CQDs at ambient temperature, FL emission intensity remains unchanged even after 6 month of incubation.	73
Figure 3.6	(a) FL emission intensity of N-CQDs at different pH range from 2 to 12, (b) emission intensity of N-CQDs towards the detection of Co^{2+} in different pH range from 2 to 12 (F_0 and F are the FL emission intensities of N-CQDs in the absence and presence of Co^{2+} , respectively). Error bar is showing the three replicate measurements.	75
Figure 3.7	(a) Ratio between the fluorescence changes after the addition of various metal ions (100 μM) including (Mn^{2+} , Al^{3+} , Cd^{2+} , Hg^{2+} , Zn^{2+} , Pb^{2+} , Co^{2+} , As^{3+} , Ca^{2+} , Mg^{2+} , Fe^{2+} , Fe^{3+} , Cu^{2+} , and Ni^{2+}) in a prepared N-CQDs whereas inset shows the photographs of vial after the addition of different metal ions in a UV light.	76
Figure 3.8	Sensitivity of the Co^{2+} in a mixture of different metals ions (100 μM), error bar shows the three independent measurement.	77
Figure 3.9	(a) Showing the FL emission spectra after the addition of different concentration of Co^{2+} (0–50 μM) in a N-CQDs, (b) reveals the plot between $F_0/F-1$ versus concentration of Co^{2+} and shows the linear correlation in a 0.5-3.0 μM range. Error bars demonstrates the standard deviation of the three replicate measurements.	78
Figure 3.10	Fluorescence spectra after the addition of AA, GSH, EDTA, and cyst into the N-CQDs/ Co^{2+} system ($[\text{AA}] = [\text{GSH}] = [\text{EDTA}]$, and $[\text{cyst}] = 1 \text{ mM}$).	80
Figure 3.11	(a) Shows the overlapping of absorbance spectrum of Co^{2+} with excitation and emission spectrum of N-CQDs, (b) fluorescence decay spectra of N-CQDs before and after incubating of Co^{2+} .	81
Figure 3.12	TEM micrograph of N-CQDs in the presence of 100 μL of Co^{2+} (100 μM).	82
Figure 3.13	Corresponding color change of N-CQDs from transparent to pale yellow after the addition of Co^{2+} (0–100 μM).	82
Figure 3.14	(a) DLS scan of N-CQDs and (b) N-CQDs/ Co^{2+} system.	83
Figure 4.1	(a, c) TEM and SAED micrograph, (b, d) XRD and FTIR spectrum of the as-synthesized N,S–CQDs.	93
Figure 4.2	XPS full survey of as-synthesized N,S–CQDs.	94

Figure 4.3	Deconvoluted XPS spectra (a) C 1s, (b) S 2p, (c) N 1s, and (d) O 1s spectra of as-synthesized N,S-CQDs	95
Figure 4.4	(a) UV-vis absorption spectrum of N,S-CQDs, (b) excitation dependent fluorescence emission spectra of N,S-CQDs after the excitation of 240, 260, 280, 300, 320, 340, 360, 380, and 400 nm), whereas inset shows the blue emission of N,S-CQDs at $\lambda_{ex}=365$ nm, (c) CIE co-ordinates obtained from the emission spectrum at 360 nm excitation, (d) fluorescence stability under the high NaCl strength (0–10 M).	97
Figure 4.5	(a) Month wise fluorescence stability of N,S-CQDs, (b) effect of pH on the fluorescence emission intensity.	98
Figure 4.6	(a) UV-vis absorption spectrum of MnO ₂ nanosheets, (b) FTIR spectra of MnO ₂ nanosheets.	99
Figure 4.7	Wide scan XPS spectrum of N,S-CQDs–MnO ₂ nanosheets	99
Figure 4.8	(a) Mn 2p spectrum, (b) O 1s spectrum of N,S-CQDs–MnO ₂ nanosheets.	100
Figure 4.9	(a, b) TEM micro-image of MnO ₂ nanosheets and N,S-CQD–MnO ₂ nano-composites, (c) fluorescence emission spectra of N,S-CQDs as a function of different MnO ₂ concentrations (0–100 μ g/mL), while inset shows the corresponding color change, and (d) the graph between the concentration of MnO ₂ nano-sheets and $(F_0-F)/F_0$ (quenching efficiency); where F_0 and F is the fluorescence emission of N,S-CQDs before and after addition of MnO ₂ nanosheets.	101
Figure 4.10	(a) The black line displays the UV-vis absorption spectrum, while red and blue indicates the excitation and emission spectrum of N,S-CQDs, respectively, (b) time resolve fluorescence decay curve of N,S-CQDs with or without MnO ₂ nano-sheets.	102
Figure 4.11	(a, b) Zeta-potential of N,S-CQDs with or without MnO ₂ nanosheets	103
Figure 4.12	Kinetics study of the fluorescence reappearance of the N,S-CQD–MnO ₂ probe in the presence of 100 μ M GSH	104
Figure 4.13	(a) Graph of cell viability assay of N,S-CQD–MnO ₂ nano-composite in A549 cells, (b) emission spectra of N,S-CQDs in association with GSH concentration from 0 to 100 μ M, inset illustrates the fluorescence image at $\lambda_{ex}=365$ nm, (c) parallel linear calibration graph between $(F-F_0)/F_0$ GSH concentrations from 0.1 to 0.7 μ M; where F_0 and F are fluorescence emission of N,S-CQDs before and after incubation of GSH into the N,S-CQD–MnO ₂ nanocomposite, and (d) selectivity of the proposed sensing system in presence of amino acids along with some other biomolecules and metal interfering agent.	106

Figure 4.14	<i>In vitro</i> cell imaging of GSH in A549 human lung cancer cells (a) Intracellular fluorescence microscopic image of A549 cells, (b and c) A549 cells incubated with N,S-CQD-MnO ₂ nanocomposite in a blue and red region, (d) corresponding bright-field image; the scale bars are 100 μm.	108
Figure 5.1	(a) Representing the TEM micrograph of CQDs whereas inset shows the size distribution by counting 34 particles, (b) SAED micrograph of CQDs, (c) XRD spectrum of CQDs at scan rate 3°/min in a range 10-80°, (d) FTIR spectrum of the as-prepared CQDs in a range 400-4000 cm ⁻¹ .	116
Figure 5.2	(a) Full scan XPS spectrum of CQDs, (b) shows the C 1s spectrum, (c) N 1s spectrum, and (d) O 1s spectrum of CQDs.	117
Figure 5.3	(a) Represents the UV-visible spectrum (black)) and emission intensity spectrum (blue) at λ _{ex} of 360 nm of N-CQDs whereas inset showing the photograph of vial under UV excitation 365 nm, (b) represents the emission intensity at different excitation wavelength (260, 280, 300, 320, 340, 360, 380, 400 nm).	118
Figure 5.4	(a) Photostability of CQDs, showing the fluorescence of CQDs remain almost same even after incubating 5 months at 4 °C, (b) stability under the high ionic strength after the addition of different concentration of NaCl (0, 10, 20, 30, 40, 50 mM).	120
Figure 5.5	(a) Represents the optimization of pH ranges from 3 to 13, showing that prepared CQDs is independent of the pH used, (b) the kinetic stability of CQDs-Hg ²⁺ system, indicating 5 min time is optimum to complete the quenching mechanism.	121
Figure 5.6	Change in FL emission intensity of CQDs solution (0.4 mg/L) at λ _{ex} = 360 nm in the presence of 50 μM various metal ions including (Al ³⁺ , Zn ²⁺ , Hg ²⁺ , Pb ²⁺ , Cd ²⁺ , Ca ²⁺ , Mg ²⁺ , Cu ²⁺ , Ni ²⁺ , Fe ²⁺ , and Fe ³⁺), whereas inset showing the photographs of vials under a UV excitation of 365 nm (F and F ₀ are the emission intensities of CQDs with the presence and absence of different metals).	122
Figure 5.7	(a) Fluorescence decay curve for the Hg ²⁺ detection analysis, (b) Interference study under various conditions [Hg ²⁺] = 0.05 mM, [Al ³⁺] = [Pb ²⁺] = [Ca ²⁺], [Mg ²⁺] = 5 mM, [Zn ²⁺] = [Cd ²⁺] = [Ni ²⁺] = [Fe ²⁺] = 10 mM, [Cu ²⁺] = [Fe ³⁺] = 0.01 mM.	124
Figure 5.8	(a) Illustrating the FL emission intensity of CQD-Hg ²⁺ system at 433 nm as a function of Hg ²⁺ concentration, (b) represents the dependence of F ₀ /F-1 on the Hg ²⁺ concentration within the linear range 0-0.1 μM. The error bar represents the standard deviation of three replicate measurements.	125
Figure 5.9	The fluorescence response of CQDs/Hg ²⁺ solution towards different essential amino acids of concentration 40 μM where F and F ₀ are fluorescence intensities of CQDs/Hg ²⁺ /amino acid and CQDs respectively.	127

- Figure 5.10** (a) FL spectra of CQDs/Hg²⁺ in the increasing concentration of GSH (0 to 40 μM), (b) showing relationship between FL of CQDs/Hg²⁺ and GSH from 0 to 20 μM. The error bars represent the standard deviation of three replicate measurements. Whereas F_a is the recovered emission intensity of CQDs in the presence of GSH, F is the FL intensity of CQDs in the presence of Hg²⁺ (50 μM), and F₀ is the emission of CQDs at 433 nm, respectively. 128
- Figure 6.1** (a) Shows the TEM micrograph of CQDs whereas inset elucidate the particle size distribution on counting 45 particles, (b) represents the SAED micrograph of the CQDs and inset shows the HRTEM micrograph at 10 nm magnification, (c) demonstrates the XRD spectrum of CQDs in a range 10-70° with a scan rate 3°/min, and (d) shows the FTIR spectra of CQDs before and after formation. 138
- Figure 6.2** Represents the wide scan spectrum of the as-prepared CQDs. 139
- Figure 6.3** (a) High resolution XPS scan of C1s, (b) N1s, (c) O1s, and (d) S2p spectra of the as-prepared CQDs. 140
- Figure 6.4** (a) UV-visible spectrum (black line) and fluorescence emission spectrum (blue line) at λ_{ex} 360 nm while inset shows the photograph of vial under UV-excitation at 365 nm in a UV-chamber and (b) shows the fluorescence emission at different excitation wavelength (280, 300, 320, 340, 360, 380, 400, and 420 nm). 142
- Figure 6.5** (a) Effect on the fluorescence emission intensity on varying pH from 2 to 12 (b) ratio of fluorescence intensity after incubating NaCl concentration (0-100 mM), where F is the fluorescence emission intensity at 450 nm after incubating NaCl salt solution and F₀ denotes the fluorescence emission intensity before the addition. 143
- Figure 6.6** (a) Shows the effect of fluorescence emission after exposing UV light for 24 hrs, (b) explores the fluorescence stability over 4 months of incubation, (c) Shows the scanned Zeta potential image of the as-prepared CQDs, (d) express the hydrophilicity of the CQDs in a mixture of water with certain classic solvent. Error bar shows the three independent repeated measurements. 144
- Figure 6.7** (a) Represents the UV-visible absorbance spectra of TMB, TMB+H₂O₂, and TMB+H₂O₂+CQDs reaction system, (b) absorbance changes at 652 nm of ox-TMB with a catalytic time course 40 min in a different reaction system TMB+CQDs, TMB+H₂O₂, and TMB+ H₂O₂+CQDs ([TMB] = [H₂O₂] = 2 mM, [CQDs] = 0.5 mg/mL) whereas inset represents the blue colored reaction of ox-TMB. 146
- Figure 6.8** (a) Represents the absorbance spectra of TMB based oxidation at different pH ranges from 2 to 6, (b) effect of temperature, (c) optimization of H₂O₂ concentration, and (d) optimization of TMB concentration on the peroxidase-mimic activity of the as-prepared CQDs. 147

- Figure 6.9** Shows the steady state kinetic analysis and catalytic mechanism of CQDs (a-d), error bars represent the standard error on measuring three repeated measurement (a) the H_2O_2 concentration was fixed at 8 mM and TMB concentration was varied from 0.08 to 6 mM whereas (b) shows the lineweaver-burk plot corresponding to fixed H_2O_2 concentration, (c) the TMB concentration was fixed at 7 mM and H_2O_2 concentration was varied from 0.08 to 1.2 mM, and (d) shows the lineweaver-burk plot corresponding to fixed TMB concentration. **149**
- Figure 6.10** (a) Shows the fluorescence emission spectra of TPAOH formed from the oxidation of TPA by $\cdot\text{OH}$ radical which was generated during the destruction of H_2O_2 on activating with CQDs and (b) shows the effect of $\cdot\text{OH}$ radical scavenger on the peroxidase-mimic activity of CQDs. **152**
- Figure 6.11** Represents the change in absorbance at 652 nm after the addition of different amino acids, GSH, gluc, AA, TA, CA, and UA (100 μM) into the TMB+ H_2O_2 +CQDs whereas inset shows the corresponding reaction color obtained during the addition ($[\text{TMB}] = 7 \text{ mM}$, $[\text{H}_2\text{O}_2] = 8 \text{ mM}$, and $[\text{CQDs}] = 0.5 \text{ mg/mL}$). Where $\Delta A = A_0 - A$, A_0 is for the initial absorbance and A for the absorbance obtained after the addition of amino acids, glucose, and GSH. **154**
- Figure 6.12** (a) Absorbance spectra of ox-TMB on increasing the GSH concentration (0-100 μM), (b) change in absorbance at 652 nm with the increased GSH concentration. Inset figure shows the linear calibration plot for the reduction of ox-TMB in a range 0.02–0.1 μM . Error bars shows the standard error on measuring three repeated measurements. **155**