CHAPTER 7

Ethylene Diamine Mediated Synthesis of Cobalt Nanoparticle Studded Graphene Oxide Quantum Dots with Tunable Photoluminescence Properties
Advances in solution phase synthesis of GQDs have served as a platform for investigation of optical and optoelectronic properties for novel applications. Consequently, they have a wide and varied range of applications such as in biological imaging and labeling, light emitting diodes, electroluminescence, organic photovoltaic devices, catalysis, and sensors etc.\textsuperscript{46,251,252} In addition, the optical properties of GQDs can be easily tailored in the visible region by controlling the size and surface functionalities on the GQDs. Solution based synthetic approach of preparation of GQDs has potential for producing large quantities of GQDs thereby opening up new opportunities for chemical functionalization. Although many surfactant based methods are available, the presence of stabilizers is often undesirable and since practical applications require the presence of functional groups, therefore development of easier ways for better dispersibility and proper functionalization of graphene materials is the need of the hour.\textsuperscript{253}

On the other hand, continuous efforts for the preparation of GQDs with high QY is very much demanding and important. Several methods such as chemical reduction and surface passivation are the most common pathways to improve the QY of GQDs and for tuning the fluorescence emission spectra of GQDs. For instance, Li et al.\textsuperscript{65} used NaBH\textsubscript{4} as reducing agent to convert greenish-yellow luminescent GQDs synthesized by microwave assisted method, to bright blue luminescent GQDs with higher QY. Shen et al.\textsuperscript{67} prepared GQDs passivated by poly(ethylene glycol) PEG, and found the QY of as-prepared GQDs-PEG with 360 nm emission was up to 28%,
which was two times higher than the pristine GQDs. Sun et al. used alcohols as the reducing agent assisted with UV irradiation to prepare bright blue luminescent GQDs with high QY through photo-reducing pathway.\textsuperscript{66} Many other techniques include amidation of carboxyl groups, ring-opening reaction of epoxide, nitrogen doping, etc. For example, GQDs surface passivated by poly(ethylene glycol) were reported to possess bright blue emission.\textsuperscript{67} The modification of alkylamine or amino groups onto GQDs tuned their emission with a blue or a red shift.\textsuperscript{212} GQDs grafted with aniline or methylene blue moieties showed efficient photovoltaic properties. The GQDs amidated with a specific recognition moiety can be applied for the optical detection of Cu\textsuperscript{2+}. Luo et al.\textsuperscript{254} modified GQDs with different aryl groups by Gomberg–Bachmann reaction. Upon the resonance effects between aryl groups and graphene basal planes, the photoluminescence (PL) properties of GQDs are tuned systematically. Moreover, the aryl-modified GQDs showed greatly improved fluorescence properties both in their QYs and pH tolerance. All the chemical functionalization methods however, are based on the use of oxygen functionalities of GQDs as reactive sites for chemical reactions.\textsuperscript{254} Therefore facile and solution based methods for increasing the photoluminescence properties of GQDs is still being explored. Photoluminescence tuning of GQDs by various other techniques tailoring interesting applications of GQDs in optoelectronics include cutting of fluorinated graphene to fluorinated GQDs with bright blue PL and clear upconversion luminescence properties as reported by Feng et al.\textsuperscript{255} by a facile hydrothermal approach for cutting preoxidized N-doped graphene into N-doped GQDs which possess excellent up-conversion photoluminescent (PL) properties in addition to bright blue PL as reported by Li et
or by amino functionalization of graphene quantum dots which led to excitation wavelength dependent tunable heterogeneous PL as reported by Kumar et al.\textsuperscript{248}

Furthermore, although a great deal of work has been done on GQDs, there are only a few reports available on synthesis of Graphene Oxide Quantum Dots (GOQDs).\textsuperscript{257,258} GOQDs have diameter in the range 3–20 nm, which paves way for a host of advantageous properties like larger surface-to-volume ratio, better solubility in both aqueous and nonaqueous solvents, higher tunability of physiochemical and photoluminescence properties, non-toxicity, better amenability to hybridize with other nanomaterials, and more ease of doping and functionalization. Therefore, GOQDs have the potential to outshine the conventional organic fluorophores and semiconductor quantum dots in bioimaging, optical sensing, and photovoltaics.\textsuperscript{259-261} In addition to being applicable in energy storage and conversion.\textsuperscript{262,263} GOQDs are known to exhibit zero-dimensional distinctive electronic and optical properties owing to their large edge effects and quantum confinement.\textsuperscript{264} Zeng et al. reported synthesis of QDs from carbon black via a hydrothermal method using covalent-surface functionalized PVDF membrane possessing attractive combined features of hydrophilicity, stability, anti-biofouling, and antibacterial properties.\textsuperscript{265} Interesting PL properties were observed by Liu et al. simply by the reduction of GOQDs at different annealing temperatures (300–900\(^\circ\)C) tailoring the PL of reduced GOQDs from blue to purple enabling its potential application in future graphene based optoelectronic devices.\textsuperscript{266} However, the differences between GOQDs and GQDs pertaining to surface groups and the related PL behaviours are almost completely unknown.\textsuperscript{258}

7.1 The Motivation
Recently graphene based composites with inorganic nanostructures, organic crystals, polymers, metal–organic frameworks (MOFs), biomaterials, and carbon nanotubes (CNTs), have been extensively explored in a wide range of applications starting from batteries, supercapacitors, fuel cells, and photovoltaic devices, to photocatalysis, sensing platforms, Raman enhancement and so on. Mombru et al. demonstrated the preparation of polyaniline–graphene oxide quantum dots nanocomposites via tuning of the electric transport dimensionality for novel electronic device applications.\textsuperscript{267} Graphene-inorganic nanohybrids have already been prepared with metals nanoparticles like Au, Ag, Pd, Pt, Ni, Cu, Ru and Rh oxides like TiO\textsubscript{2}, ZnO, SnO\textsubscript{2}, MnO\textsubscript{2}, Co\textsubscript{3}O\textsubscript{4}, Fe\textsubscript{3}O\textsubscript{4}, NiO, Cu\textsubscript{2}O, RuO\textsubscript{2}, and SiO\textsubscript{2}; and chalcogenides like CdS and CdSe. The fabrication methods for such composites fall into two categories viz. \textit{ex situ} hybridization, and \textit{in situ} crystallization. \textit{Ex situ} hybridization involves the mixing of premodified graphene nanosheets with commercially available nanocrystals via non-covalent interactions or chemical bonding. However, it sometimes suffers from the drawback of low density and non-uniform coverage of the nanostructures on the Graphene Oxide (GO)/Reduced Graphene Oxide (rGO) surfaces. On the contrary the \textit{in situ} crystallization leads to uniform surface coverage of nanocrystals by controlling the nucleation sites on GO/rGO via surface functionalization thereby giving rise to a continuous film of nanoparticles (NPs) on graphene surfaces. In \textit{in situ} method involves the reduction of metal precursors using various reducing agents like amines, NaBH\textsubscript{4}, and ascorbic acid. Few commonly used techniques for \textit{in situ} synthesis of metal nanoparticles on graphene surfaces include microwave irradiation, sol–gel process, hydrothermal process, electrochemical deposition etc.\textsuperscript{268} For instance, HRG/Au nanocomposites were prepared by reduction of HAuCl\textsubscript{4} with NaBH\textsubscript{4}\textsuperscript{269} and
graphene-based bimetallic HRG/Pt/Pd nanocomposites were synthesized by in situ reduction of H₂PdCl₄ and K₂PtCl₄ with HCOOH and ascorbic acid.²⁷⁰ Ji et al. demonstrated a facile method for the preparation of HRG/Co nanocomposites and also demonstrated their magnetic properties.²⁷¹ The integration of metal nanomaterials into graphene can therefore further optimize and efficiently enhance the optical properties of graphene materials as well as improve their applications in a wide variety of fields.²⁷² For instance, Cao et al. reported the synthesis of a graphene–CdS quantum dot nanocomposite and studied the ultrafast electron transfer process from the excited CdS to the graphene sheet by time-resolved fluorescence spectroscopy demonstrating the potential optoelectronic applicability of this new type of graphene-based semiconductor hybrid system.²⁷³

Although a great deal of work has been done regarding the formation of graphene-inorganic metal nanoparticle composites, as far as our knowledge is concerned the area of GOQDs-inorganic nanoparticle hybrid via in situ formation of metal nanoparticles on GOQDs is yet to be explored. This is due to the small interlayer spacing in graphene (0.34 nm) that it becomes challenging to incorporate nanoparticles into the spaces between the layers. In this case the use of ions becomes handy with the advantages of small size, easy incorporation into the spacings followed by reduction/oxidation to form nanoparticles. Introducing the nanoparticles incorporates defects in the graphene material giving rise to interesting physico-chemical properties. In the present study we report a simple method for one step reduction cum functionalization of GOQDs using ethylene diamine followed by ethylene diamine mediated immobilization of Co²⁺ within the graphene layers and also at the surface and formation of cobalt oxide nanoparticles (Co₃O₄ NPs). We
chose cobalt chloride as the precursor for nanoparticle synthesis with a view that Co$^{2+}$ ions can easily enter the interlayer spacings between the graphene layers. Moreover, as we chose ethylene diamine as the reducing agent and it is well known to form stable complex with Co$^{2+}$, therefore, this acted as the driving force for immobilization of Co$^{2+}$ on the GOQDs. Further the changes observed upon successful functionalization and in situ nanoparticle formation were monitored using different analytical techniques with special inference from fluorescence spectroscopy, the aspect which has not been much studied for graphene-based inorganic metal nanoparticle composites. Insight into the reversible on/off fluorescence switching property of the functionalized GOQDs is also being provided with quite satisfactory results upto three consecutive oxidation–reduction cycles.

7.2 Materials

Commercially available graphene platelet nanopowder (GPN Type 1, thickness 6–8 nm) (Sisco Research Laboratories Pvt. Ltd.), ethylene diamine (≥98%) (Merck Specialities Pvt. Ltd.), hydrogen peroxide (H$_2$O$_2$) solution (50%) (Merck Specialities Pvt. Ltd.), concentrated sulfuric acid (H$_2$SO$_4$) (98%) (Merck Specialities Pvt. Ltd.), concentrated nitric acid (HNO$_3$) (70%) (Merck Specialities Pvt. Ltd.), cobalt (II) chloride hexahydrate (CoCl$_2$.6H$_2$O) (Merck Specialities Pvt. Ltd.), nickel (II) chloride hexahydrate (NiCl$_2$.6H$_2$O) (Merck Specialities Pvt. Ltd.) and copper (II) sulphate pentahydrate (CuSO$_4$.5H$_2$O) (Merck Specialities Pvt. Ltd.) were used as received without further purification. The water used throughout the experiments was from a Milli-Q water purification system.
7.3 Experimental

7.3.1 Synthesis of Graphene Oxide Quantum Dots (GOQDs) from Graphene Platelet Nanopowder

Commercially available graphene platelet nanopowder was exfoliated and oxidized in a single step using an acid mixture oxidant i.e., a 3 : 1 mixture of concentrated H$_2$SO$_4$/HNO$_3$ by using a simple sonication and centrifugation technique at room temperature. Briefly, a 50 mL dispersion of graphene platelet nanopowder was prepared by dispersing 0.01 g of graphene platelet nanopowder in the acid mixture oxidant. This mixture was then sonicated for a time period of 24 hours in a bath sonicator. After sonication the dispersion was diluted by adding 100 mL of deionized water and centrifuged at 2500 rpm for 45 minutes to separate the lighter exfoliated graphene nanoplatelets. The supernatant solution was then separated from the heavier particles and washed thoroughly with millipore water and was subsequently characterized. This dispersion contained small particles of exfoliated and oxidized graphene oxide and was termed as the graphene oxide quantum dot (GOQDs) solution. The concentration of GOQDs in solution was approximately determined to be 0.66 mgmL$^{-1}$.

7.3.2 One-step Reduction and Functionalization of GOQDs with Ethylene Diamine (en)

The GOQDs synthesized in the previous step were oxidized and functionalized in a single step using ethylene diamine mediated reduction. Typically, 10 mL of the as-prepared GOQDs solution was taken in a round bottom flask and to it 15 mL of 33% ethylene diamine solution was added with continuous stirring. The pH of the
reaction mixture was adjusted at around 10 and was refluxed for 8 hours at 80°C accompanied with continuous stirring. The color of the reaction mixture gradually turned to bright yellow. The mechanism of reduction and functionalization of GOQDs by ethylene diamine via ring opening of epoxy groups had already been reported earlier. The proposed mechanism for the reduction of GOQDs by ethylene diamine occurred via reaction of diamine with epoxy groups via a ring opening addition reaction; the driving force for the reaction being the strain on the three-membered epoxy ring which always has a tendency to open up. Further, some of the amine groups would also react with the carboxylic acid groups on the GOQDs to form covalent amide linkages thereby leading to covalent functionalization. The GOQDs reduced and functionalized with ethylene diamine were termed as GOQDs-en solution. The concentration of GOQDs-en in solution was found to be approximately 0.44 mgmL⁻¹.

7.3.3 Ethylene Diamine Mediated in situ Synthesis of Co₃O₄NPs on GOQDs-en

The GOQDs reduced and functionalized by ethylene diamine (GOQDs-en) was used as a medium for the in situ synthesis of cobalt nanoparticles. Typically, 8 mL of the reduced GOQDs-en solution was taken in a round bottom flask and to it 2 mL of 2 mM cobalt chloride hexahydrate solution (CoCl₂.6H₂O) was added and stirred magnetically at room temperature for 30 minutes. The color of the solution turned to slightly brown. Subsequently, to this solution 4 mL of 30% H₂O₂ solution was added drop wise with continuous stirring and the reaction mixture was refluxed for 8 hours at 80°C. This sample was termed as GOQDs-en-Co₃O₄NPs solution.
7.4 Characterization

The graphene platelet nanopowder was dispersed in the acid mixture oxidant and subjected to sonication using a bath sonicator Hwashin Technology Company Powersonic 603. The prime characteristic property of quantum dots being their particle sizes below 10 nm, the particle size and zeta potential measurements of the prepared samples were carried out on a Malvern Zetasizer Nanoseries, Nano-ZS90. The surface morphology and the elemental analysis of the GOQD samples were investigated via Scanning Electron Microscopy (SEM) and also via Transmission Electron Microscopy (TEM) using a Carl Zeiss (Sigma VP) instrument and JEOL, Model: JEM 2100 respectively. Powder X-ray diffraction (XRD) spectra were collected on a Bruker D8 Advance diffractometer. Raman spectra were collected on a STR Series Raman Spectrometer (STR 300) with a 532 nm excitation laser. pH measurements of the samples were carried out on an Accumet Excel Dual Channel pH/Ion/Conductivity Meter, XL 50 (Fischer Scientific). UV-visible absorption spectra were collected on a Shimadzu UV-VIS Spectrophotometer, UV-2600. Optics Technology UV lamp (365 nm) was used to check the fluorescence intensity of the GOQDs samples. The characteristic photoluminescence spectra of the samples were collected on a Varian Cary Eclipse Spectrofluorometer. Further, in order to confirm the successful incorporation of different functionalities on the GOQDs surface before and after surface functionalization, the Fourier Transform infrared (FT-IR) spectra were recorded on a Nicolet-6700 FT-IR spectrophotometer. The spectra were obtained using KBr pellet samples in transmission mode over 32 scans in the range of 400-4000 cm\(^{-1}\).
7.5 Results and Discussion

Commercially available graphene platelet nanopowder was exfoliated and oxidized in a single step using an acid mixture oxidant i.e., a 3 : 1 mixture of H_2SO_4/HNO_3 by using a simple sonication and centrifugation technique at room temperature as described in the experimental section. This procedure had already been reported to produce oxygen functionalities on all kinds of nanocarbon materials. The reactive species of the process responsible for the oxidation was the nitronium ion (NO_2^+) which was generated in situ as given by the following equation:

\[
H_2SO_4 + HNO_3 = HSO_4^- + NO_2^+ + H_2O
\]

Scheme 7.1 The schematic representation of the complete process of oxidation-exfoliation of graphene nanoplatelets to form GOQDs, reduction-functionalization of GOQDs to form GOQDs-en and ethylene diammine aided in situ formation of Co_3O_4 NPs to give GOQDs-en-Co_3O_4 NPs.
The dispersion of GOQDs prepared by the above procedure was yellow in colour. GOQDs prepared by the above procedure were then subsequently reduced and functionalized in a single step with ethylene diamine (en) to give amine functionalized GOQDs i.e., GOQDs-en and finally the GOQDs-en sample was used as a medium for the in situ synthesis of cobalt nanoparticles.

The schematic representation of the complete process of oxidation-exfoliation of graphene nanoplatelets to form GOQDs, reduction-functionalization of GOQDs to form GOQDs-en and in situ formation of Co$_3$O$_4$NPs to give GOQDs-en-Co$_3$O$_4$NPs nanocomposite is illustrated in Scheme 7.1.

7.5.1 Characterization of the Quantum Dot Samples Prepared

The materials synthesized viz. GOQDs, GOQDs-en and GOQDs-en-Co$_3$O$_4$NPs were subsequently subjected to stepwise and systematic characterization to confirm the presence of characteristic properties.

(a) Inference from Dynamic Light Scattering (DLS) Analysis

The particle sizes and zeta potential values of the prepared samples viz. GOQDs, GOQDs-en and GOQDs-en-Co$_3$O$_4$NPs were determined from dynamic light scattering (DLS) measurement. The particle size distribution graphs and zeta potential values of all the three samples prepared are shown in Figure 7.1 (A), (B) and (C) respectively.
Figure 7.1 The particle size distribution graphs and zeta potential values of (A) GOQDs, (B) GOQDs-en and (C) GOQDs-en-Co₃O₄NPs as obtained from Dynamic Light Scattering (DLS) measurements.

Figure 7.1 shows the particle size distribution graphs of the prepared samples viz. GOQDs, GOQDs-en and GOQDs-en-Co₃O₄NPs. It is to be observed that all the three samples were found to exhibit average particle size diameters below 10 nm i.e., 4.9 nm, 1.074 nm and 6.8 nm respectively for GOQDs, GOQDs-en and GOQDs-en-Co₃O₄NPs respectively thereby providing preliminary evidence for formation of quantum dot systems. The zeta potential values of the systems were also determined and were found to be negative for all the three samples. However, it was to be noted that the value of zeta potential for GOQDs observed to be -2.6 mV was subsequently changed to -12.8 mV upon formation of GOQDs-en due to increased electron density upon formation of –OH groups via ring opening of epoxy groups by ethylene diamine and formation of –NHCH₂–CH₂–NH₂ linkages. Formation of Co₃O₄NPs again led to an increase in the zeta potential value to -4.51 mV, indicating a decrease in the electron density due to elimination of some –NH₂ groups as ammonia on addition of H₂O₂ to form Co₃O₄NPs.

(b) Inference from Energy Dispersive X-ray (EDX), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) Analysis
The surface morphology and size of the GOQDs prepared was further studied using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

**Figure 7.2** Stacked SEM, TEM micrographs and EDX spectra of (A) GOQDs, (B) GOQDs-en and (C) GOQDs-en-Co$_3$O$_4$NPs and (D) table showing the respective weight percentages of different elements present in the samples as obtained from EDX analysis.

Figure 7.2 (A), (B) and (C) shows the stacked SEM, TEM micrographs and EDX spectra of GOQDs, GOQDs-en and GOQDs-en-Co$_3$O$_4$NPs respectively along with the respective weight percentages of different elements present in the samples as tabulated in Table 7.1.

Figure 7.2 (A) shows the SEM and TEM micrographs and the EDX spectrum of GOQDs. From the micrographs it was very well evident that the particle sizes of GOQDs were below 10 nm which was in accordance with that observed from DLS technique as shown in Figure 7.1 (A). Further, elemental analysis results tabulated in Table 7.1 showed the presence of the elements C (7.65%) and O (3.94%) in the GOQD sample. The presence of oxygen in the EDX spectra for GOQDs indicated
the successful incorporation of oxygen functionalities on the surface of the graphene sheets upon acid mixture oxidation of graphene nanoplatelets. In a similar manner, Figure 7.2 (B) shows the SEM and TEM micrographs and the EDX spectrum of GOQDs-en. SEM and TEM micrographs showed the presence of particles below 10 nm. On the other hand the EDX spectrum showed the presence of the elements C (9.35%), O (1.25%) and N (1.82%). The presence of nitrogen gave a clear indication of formation of C-NH linkages on the sheets due to formation of amide functionality and en attachment to the sheet structure via ring opening of epoxy groups. Moreover, it was interesting to note that the weight percentage of oxygen in GOQDs was found to decrease upon reduction and functionalization with en which could probably be attributed to the conversion of –COOH groups on the GOQDs to –CONH₂ upon reaction with ethylene diammine. Similarly, Figure 7.2 (C) shows the SEM, TEM micrographs and EDX spectrum of GOQDs-en-Co₃O₄NPs. The images showed particles in the range 5–15 nm in size which had already been confirmed from DLS analysis as shown in the Figure 7.1 (C). In order to confirm the formation of Co₃O₄NPs on GOQDs-en, EDX analysis was carried out. The EDX spectrum clearly showed the presence of the elements C (15.31%), N, O (0.59%) (1.09%) and Co (0.04%) as shown in Table 7.1. From the table it was observed that the weight percentages of oxygen decreased upon reduction and functionalization with en which was consistent with the conversion of –COOH groups on the sheet surface to form –CONH₂. Further, after formation of Co₃O₄NPs, the weight percentage of nitrogen was decreased to half and this was consistent with the liberation of N atoms as ammonia upon addition of H₂O₂ to form Co₃O₄NPs. The remaining 0.59% N indicated the presence of –CONH₂.
groups on the surface of GOQDs-en. Therefore EDX analysis provided convincing evidence for the successful oxidation, reduction and functionalization and formation of Co$_3$O$_4$NPs on GOQDs.

(c) Inference from UV-Visible Spectroscopic Analysis

GOQDs, ethylene diamine reduced and functionalized GOQDs (GOQDs-en) and that after formation of cobalt oxide nanoparticles (GOQDs-en-Co$_3$O$_4$NPs) were characterized by UV-visible spectroscopy. The stacked UV-visible spectra of GOQDs, GOQDs-en, GOQDs-en-Co$_3$O$_4$NPs and pure cobalt chloride (CoCl$_2$·6H$_2$O) is shown in Figure 7.3.

![Figure 7.3](image)

Figure 7.3 (A) Stacked UV-visible absorption spectra of GOQDs, ethylene diamine reduced GOQDs (GOQDs-en), that after formation of cobalt oxide nanoparticles (GOQDs-en-Co$_3$O$_4$NPs) and of pure cobalt chloride (CoCl$_2$). Inset shows the d–d transition band in CoCl$_2$ which did not appear for GOQDs-en-Co$_3$O$_4$NPs. (B) The various peak positions obtained in the UV-Visible spectra of GOQDs, GOQDs-en and GOQDs-en-Co$_3$O$_4$NPs along with the respective peak assignments are tabulated in Table 7.2.

The UV-Visible absorption spectrum of GOQDs was found to exhibit two distinct peaks viz. at ~230 nm and ~300 nm. The peak near 230 nm could be assigned to $n\rightarrow\sigma^*$ transition of the –OH, epoxy and –COO’ groups arising due to oxidation...
whereas the other peak near 300 nm could be assigned to $\pi \rightarrow \pi^*$ transition of the C=C bond. The presence of these two peaks for the oxidized sample indicated the successful oxidation of graphene nanoplatelets. Again for ethylene diamine reduced GOQDs, the absorbance of the 300 nm peak was considerably reduced with a tail extending into the visible region which indicate the successful reduction of GOQDs by ethylene diamine. Further upon titration with Co$^{2+}$ ions in solution, the peak at ~230 nm was found to be hypsochromically shifted to 224 nm and also the peak at ~300 nm observed for ethylene diamine reduced GOQDs was found to completely disappear indicating successful coordination of amine groups of en to Co$^{2+}$ ions. However, upon reduction and Co$_3$O$_4$ NPs formation, this peak was found to be reduced in intensity. After Co$_3$O$_4$NPs formation the intensity of the peak was found to be further reduced due to the fact that some of the –NH$_2$ groups of ethylene diamine and –CONH$_2$ groups were being liberated as ammonia upon addition of H$_2$O$_2$ thus further decreasing the number of possible $\pi \rightarrow \pi^*$ transitions.

The coordination between the amine groups of ethylene diamine and Co$^{2+}$ ions resulted in color change from light pink (CoCl$_2$.6H$_2$O solution) to light brown (CoCl$_2$/en solution). The UV-visible absorption spectrum of cobalt chloride hexahydrate was found to exhibit a d–d absorption band at 520 nm as shown in inset of Figure 7.3 (A). However, this characteristic band was absent in the spectrum of GOQDs-en-Co$_3$O$_4$NPs nanocomposite indicating that there were no free CoCl$_2$ in the solution. Thus, UV-Visible spectroscopy could provide convincing evidence of successful oxidation, reduction cum functionalization and in situ formation of Co$_3$O$_4$NPs on GOQDs-en.
Figure 7.4 Stacked UV-Visible titration spectra for successive addition of (A) Co$^{2+}$, (B) Ni$^{2+}$ and (C) Cu$^{2+}$ to GOQDs-en.

Additionally, in order to confirm the complex formation between Co$^{2+}$ ions and en reduced GOQDs i.e., GOQDs-en, titration experiments were carried out and monitored via UV-Vis spectroscopy. For this experiment, 2.5 mL of GOQDs-en solution was taken in a quartz cuvette and its absorption spectrum was recorded. Subsequently, different concentrations of Co$^{2+}$ solution was added to the cuvette and the corresponding absorption spectra were recorded. The experiment was repeated in a similar manner for Ni$^{2+}$ and Cu$^{2+}$ ions. Figure 7.4 shows the stacked UV-Visible absorption spectra for titration of GOQDs-en solution with different concentrations of (A) Co$^{2+}$, (B) Ni$^{2+}$ and (C) Cu$^{2+}$ ions. The titration curve with Co$^{2+}$ showed that the intensity of the peak ~300 nm of GOQDs-en gradually increased in intensity as the concentration of Co$^{2+}$ increased and reached saturation at a concentration of 460 mM Co$^{2+}$. Further, a new absorption peak was found to appear at ~375 nm with absorbance increasing with concentration of Co$^{2+}$ ions added. However, no such increase in absorbance was observed for GOQDs-en upon addition of Ni$^{2+}$ and Cu$^{2+}$ in the same concentration range. This provided a clear indication of the successful coordination of GOQDs-en exclusively with Co$^{2+}$. 
(d) Inference from FTIR Spectroscopy and Powder XRD Analysis

FTIR spectroscopy further pointed towards successful ethylene diamine mediated formation of Co$_3$O$_4$NPs on GOQDs-en. Figure 7.5 (A) shows the stacked FTIR spectra of (a) graphene nanoplatelets before oxidation (b) GOQDs (c) en (d) GOQDs-en and (e) GOQDs-en-Co$_3$O$_4$NPs. The FTIR spectrum of graphene showed peaks at 2924, 2855 cm$^{-1}$ (–C–H stretching vibration) and at 1507 cm$^{-1}$ (–C–C stretch; aromatics). The spectrum for GOQDs showed peaks at 3191 cm$^{-1}$ (O–H stretch), 1748 cm$^{-1}$ (C=O stretch), 1508 cm$^{-1}$ (C–C (in ring) aromatics), 1455 (C–H bend), 1293, 1171 cm$^{-1}$ (C–O stretch; alcohol, carboxylic acid, ether), 1004 cm$^{-1}$ (=C–H bend) and 550 cm$^{-1}$ (C–H aromatics). The spectrum of GOQDs when compared with that of pristine graphene nanoplatelets showed the successful oxidation and incorporation of different functional groups into the graphene nanoplatelets. On the other hand peaks for ethylene diamine (en) were found to appear at 3290 cm$^{-1}$ (N–H stretch 1º amine), 3043 cm$^{-1}$ (C–H stretch alkanes), 1667 cm$^{-1}$ (N–H bend 1º amine), 1329 cm$^{-1}$ (C–H rock alkanes), 1179, 1063 cm$^{-1}$ (C–N stretch aliphatic amine) and 947 cm$^{-1}$ (N–H wag 1º amine). Upon reduction cum functionalization of GOQDs with ethylene diamine, the peak positions appeared at 3040 cm$^{-1}$ (C–H stretch alkanes), 1570 cm$^{-1}$ (–NH$_2$ bending), 1380 cm$^{-1}$ (N–H stretch 1º amine), and 1100 cm$^{-1}$ (C–N stretch). The absence of the peak at 1748 cm$^{-1}$ (C=O stretch for carboxylic acid), and 1171 cm$^{-1}$ (C–O stretch) for GOQDs-en gave a clear indication of the interaction of en with –COOH groups to form amide linkages and ring opening of epoxy groups to form –OH and –NHR groups on GOQDs-en. Further, upon formation of Co$_3$O$_4$NPs on GOQDs-en as proposed, the peak positions were found to appear at 3040 cm$^{-1}$ (C–H stretch alkanes), 1670 cm$^{-1}$
(stretching mode of amide), 1570 cm\(^{-1}\) (\(\text{–NH}_2\) bending), 1380 cm\(^{-1}\) (C=C) and the peak at 1100 cm\(^{-1}\) (C–N stretch) was shifted to 1120 cm\(^{-1}\) after formation of Co\(_3\)O\(_4\)NPs.

Further support for successful ethylene diamine mediated in situ formation of Co\(_3\)O\(_4\) NPs on GOQDs-en could be drawn from powder XRD analysis of GOQDs, GOQDs-en and GOQDs-en-Co\(_3\)O\(_4\)NPs as shown in Figure 7.5 (B). The diffractogram for GOQDs showed diffraction peak at \(2\theta = 25.5^\circ\) (002) corresponding to the disorderedly stacked graphene sheets\(^{277}\) upon oxidation to form GOQDs (the GOQDs prepared were not monolayer and might possess a few layers of stacked graphene with a well-defined lattice structure). The spectrum of GOQDs-en showed sharp and well-defined peaks at \(2\theta\) values of 12.76 (110), 15.6
(221), 25.5 (002) and 38.9 (-290) degrees. Apart from the peak at 25.5° (002) characteristic of graphene, the other peaks in the sample were found to match the diffraction patterns of 1,8-Bis(dimethylamino)naphthalene-3-hydroxy benzoic acid (JCPDS Number 00-059-1052), 4’-(aceto-N’-(2-naphthylloxymethylcarbonyl)hydrazone)benzo-15-crown-5 (JCPDS Number 00-056-1881) and 3,3’-dimethyl-4,4’-bis(2,4-dinitroanilino)biphenyl (JCPDS Number 00-056-1866). As these compounds were all aromatic amino compounds, we could conclude that in GOQDs-en the peaks occurred probably due to incorporation of amine functional groups into the planar structure of the GOQDs and therefore GOQDs-en resembled the structure of the above mentioned compounds. Further, as the amine we had used was ethylene diamine, an aliphatic amine, thus it pointed more towards the possibility of the peaks appearing due to amine functionalization of GOQDs to give GOQDs-en. Thus it could be inferred as an indication of successful incorporation of –NH₂ groups into the GOQDs. On the other hand diffraction peaks appearing at 2θ = 19.7° (111), 31.5° (220) and 38.8° (311) along with the (002) peak for GOQD-en-Co₃O₄NPs could be ascribed to the well-crystallized Co₃O₄ with a face-centered cubic structure.²⁷⁸

(e) Inference from Raman Spectroscopic Analysis

In order to investigate the successful oxidation, amine reduction with functionalization of GOQDs and cobalt coordination to form nanoparticles on the amine reduced GOQDs, we recorded the Raman spectra of all the prepared samples. Figure 7.6 (A) shows the stacked Raman spectra of GOQDs, GOQDs-en and GOQDs-en-Co₃O₄NPs along with the respective bands and their positions for
the different samples as tabulated in Table 7.3.

From the plot it was very well evident that the Raman spectrum for GOQDs showed two distinct peaks viz. the D and G band at 1334 and 1598 cm\(^{-1}\) respectively. The appearance of the D peak at 1334 cm\(^{-1}\) for GOQDs gave an indication of the disordered structure of graphene to form GOQDs due to oxidation by the acid mixture. However, after reduction cum functionalization by ethylene diamine i.e., for GOQDs-en the D and G peaks were found to appear at 1357 and 1587 cm\(^{-1}\) respectively.

![Figure 7.6](image_url)

**Figure 7.6** The stacked Raman spectra of GOQDs, GOQDs-en and GOQDS-en-Co\(_3\)O\(_4\)NPs showing the characteristic D and G bands. (B) Table 7.3 showing the positions at which the respective D and G bands occur in the Raman spectrum of GOQDs, GOQDs-en and GOQDS-en-Co\(_3\)O\(_4\)NPs along with the intensity ratios of the bands.

More interestingly, upon formation of cobalt oxide nanoparticles, i.e., for GOQDs-en-Co\(_3\)O\(_4\)NPs, the two characteristic peaks were found to appear at 1335 and 1548 cm\(^{-1}\).
cm$^{-1}$ respectively. Additionally, it was to be observed that there was a shift in the peak positions of all the three samples as compared to each other. This shifting of the D and G bands indicated the successful functionalization and interaction of amine functionalized reduced GOQDs and Co$_3$O$_4$NPs. Further, the ratio between the intensities of characteristic bands i.e. I$_D$/I$_G$ gave indication about the functional group insertion. Therefore, as observed from the spectrum the decreased I$_D$/I$_G$ ratio of GOQD-en as compared to GOQDs provided evidence for the reduction of GOQDs by ethylene diamine, which reduced the number of defects on the surface of the GOQDs as well as stabilizes the GOQDs by entering into the interlayer spaces via ring opening of the epoxy groups. The subsequent increase in the I$_G$/I$_D$ ratio for GOQDs-en-Co$_3$O$_4$NPs indicated the creation of more defects after attachment of Co$_3$O$_4$ to GOQDs-en. Therefore, Raman spectroscopy provided quite convincing evidence of the entire process of oxidation, reduction cum functionalization and in situ formation of cobalt oxide nanoparticles on the GOQDs system.

(f) Inference from Photoluminescence (PL) Spectroscopic Analysis

As all the prepared samples exhibited particle sizes below 10 nm in diameter, therefore they were expected to exhibit the characteristic properties of quantum dots. The most interesting property of quantum dots being their photoluminescence properties, all the prepared GOQD samples were subjected to careful and systematic photoluminescence investigation. GOQDs synthesized were found to exhibit a broad excitation wavelength dependent PL emission spectra with a maximum emission at ~530 nm for a $\lambda_{\text{exc}} = 360$ nm. The PL from GOQDs
had been reported to originate from the combined effect of intrinsic and defect emission although it is still a matter of considerable debate.\textsuperscript{283} Successful coordination of amine groups of ethylene diamine of GOQDs-en to Co\textsuperscript{2+} was also monitored by fluorescence spectroscopy. Figure 7.7 (A) shows the stacked photoluminescence spectra of GOQDs, GOQDs-en and that after titration of GOQDs-en with cobalt chloride hexahydrate solution. It was to be observed that the GOQDs solution upon excitation at 360 nm exhibited maximum emission at ~530 nm. This emission was found to be considerably enhanced upon reduction and functionalization of GOQDs with ethylene diamine accompanied with a huge blue shift in the emission maxima. For a $\lambda_{\text{exc}} = 360$ nm, the GOQDs-en solution showed maximum emission at ~450 nm. This significant blue shift in emission maxima of GOQDs after reduction and functionalization with ethylene diamine as had been reported earlier for similar cases\textsuperscript{263,284} could probably be attributed to radiative recombination of localized electron–hole pairs within isolated sp\textsuperscript{3} clusters which in addition to size, surface effects and presence of O-containing groups; contributed to the observed blue shift of PL emission upon functionalization. Further, this emission was found to be quenched gradually upon titration with Co\textsuperscript{2+} solution in the concentration range 10–360 $\mu$M.
Figure 7.7 (A) Stacked photoluminescence spectra of GOQDs, en reduced GOQDs (GOQDs-en) and that after titration with cobalt chloride hexahydrate solution (B) Images of GOQDs and GOQDs-en under normal and UV light showing enhanced fluorescence intensity of GOQDs upon amine functionalization.

The PL quenching of GOQDs-en solution upon Co$^{2+}$ addition might be attributed to electron transfer from –NH$_2$ groups of ethylene diamine to Co$^{2+}$ as had been reported earlier for similar systems. The photoinduced charge transfer might probably led to a perturbation of electronic states of GOQDs-en thereby facilitating non-radiative transitions. This quenching in fluorescence intensity could very well be considered as an indication of successful coordination of amine groups of GOQDs-en with Co$^{2+}$. Figure 7.7 (B) shows the images of GOQDs and ethylene diamine (en) reduced GOQDs (GOQDs-en) under normal and UV light showing enhanced fluorescence intensity of GOQDs upon functionalization and reduction with ethylene diamine.

Further, in order to check the selectivity of the ethylene diamine reduced GOQDs towards Co$^{2+}$ complexation, we performed similar titration experiments with Ni$^{2+}$ and Cu$^{2+}$. It was observed that, whereas, upon Co$^{2+}$ addition, the fluorescence intensity of the ethylene diamine-reduced GOQDs was found to be quenched, no such quenching was found with either Ni$^{2+}$ or Cu$^{2+}$. The corresponding stacked photoluminescence spectra of GOQDs, en reduced GOQDs and that after titration with Ni$^{2+}$ and Cu$^{2+}$ solution is shown in Figure 7.8 (A) and (B) respectively. As evident from the figure there was no considerable change in the PL intensity of GOQDs-en upon titration with either of Ni$^{2+}$ or Cu$^{2+}$ which suggested that there was probably no complexation between en and either of Ni$^{2+}$ or Cu$^{2+}$. However, it was still not clear why only Co$^{2+}$ showed such a phenomenon exclusively.
In view of the off-on-off fluorescence behavior of the GOQDs:GOQDs-en:GOQDs-en-Co$^{2+}$ systems, we decided to study the fluorescence properties of the systems again after formation of cobalt oxide nanoparticles. Figure 7.9 (A) shows the stacked PL spectra of GOQDs, GOQDs-en and GOQDs-en-Co$_3$O$_4$NPs. It was observed that the PL intensity of GOQDs which was enhanced considerably upon amine reduction and functionalization to form GOQDs-en was further enhanced upon formation of cobalt oxide (Co$_3$O$_4$) nanoparticles along with a marked blue shift in the emission maximum at the same excitation wavelength i.e., 360 nm. The emission maxima for GOQDs, GOQDs-en and GOQDs-en-Co$_3$O$_4$NPs was found to be ~525 nm, 450 nm and 380 nm respectively for $\lambda_{\text{exc}} = 360$ nm.
Figure 7.9 (A) Stacked PL emission spectra of GOQDs, GOQDs-en and GOQDs-en-Co$_3$O$_4$NPs showing a gradual blue-shift in the emission maxima for excitation at 360 nm. (B) The images of (a) GOQDs, (b) GOQDs-en and (c) GOQDs-en-Co$_3$O$_4$NPs under normal and UV light showing the increase in fluorescence intensity of the samples from left to right accompanied with a considerable amount of blue shift.

Figure 7.9 (B) shows the images of (a) GOQDs, (b) GOQDs-en and (c) GOQDs-en-Co$_3$O$_4$NPs under normal and UV light. From the images it was quite clear that the fluorescence intensity of the samples increased from left to right accompanied with a considerable amount of blue shift as evident from the PL emission spectra. PL evolution of GOQDs could probably be attributed to the reduction of intrinsic state emissions and increase in the defect state emission. The size of sp$^2$ clusters and defect state density in GOQDs might be altered via functionalization. As the band gap of GOQDs is proposed to increase as size decreases$^{287}$ amine functionalization was proposed to tune the band gap structure of GOQDs via charge transfer or by forming an inter-band state resulting in shift of PL emission. The blue shift in the PL emission maxima might be attributed to the change of isolated sp$^2$ clusters within the C–O sp$^3$ matrix due to delocalization of electron–hole pairs, the smaller size and higher concentration of sp$^2$ clusters contributing to the energy blue-shift and intensity enhancement.$^{255,266}$ Further the enhancement of PL intensity could probably be related to the replacement of the –COO$^-$ and epoxy groups by –NHR which would otherwise induce non-radiative recombinations.$^{287}$ Upon formation of Co$_3$O$_4$NPs there was a further increase in the amine density on GOQDs which was proposed to arise due to setting free of the cobalt co-ordinated amine groups leading to further enhancement in PL intensity and blue-shift of PL energy.$^{286}$
Further, in order to investigate the selectivity of the GOQDs-en sample towards in situ formation of Co$_3$O$_4$NPs we carried out similar experiments with Ni$^{2+}$ and Cu$^{2+}$ ions to check if there was a change in the fluorescence emission property of GOQDs-en. The corresponding comparative PL emission spectra after reaction with Ni$^{2+}$ and Cu$^{2+}$ ions and their oxidation to form nanoparticles in a similar process as for Co$^{2+}$, are shown in Figure 7.10 (A) and (B) respectively. From the spectra it was very much clear that there was no further enhancement in PL intensity of GOQDs-en system after formation of Ni or Cu nanoparticles by the same procedure as adopted for Co$_3$O$_4$NPs formation. Rather there was observed quenching of PL intensity at the same value of $\lambda_{\text{exc}} = 360$ nm and also there was no considerable blue shift observed. This suggested that probably Ni and Cu nanoparticles were not formed on GOQDs-en by this process thereby demonstrating the selectivity of the GOQDs-en system for in situ synthesis of Co$_3$O$_4$NPs.

7.5.2 Investigation of Reversible On/Off Photoluminescence Behaviour: Reversibility Studies
Owing to the PL switching behaviour of GOQDs-en and GOQDs-en-Co$_3$O$_4$NPs we decided to study the reversibility behaviour of this system in order to monitor the restoration of PL intensity.

![Figure 7.11](image_url)

**Figure 7.11** (A) Reversibility graph for the consecutive oxidation–reduction of GOQDs-en upto three consecutive cycles. (B) Tabulation of percentage restoration of PL intensities after successive successive oxidation-reduction of GOQDs-en with Co$^{2+}$ upto three consecutive cycles. (C) Images of the samples after each successive oxidation and reduction step under normal and UV-light.

Figure 7.11 (A) shows the reversible PL switching cycle of (a) GOQDs-en, (b) GOQDs-en-Co$_3$O$_4$NPs and (c) after re-reduction of GOQDs-en-Co$_3$O$_4$NPs with en to release Co$^{2+}$ upto three consecutive cycles. Re-reduction of GOQDs-en-Co$_3$O$_4$NPs resulted in a decrease of PL intensity as represented by point (c) in Figure 7.11. Further, re-oxidation with H$_2$O$_2$ caused an enhancement in the PL intensity point (d) due to reformation of Co$_3$O$_4$ NPs and so on (e)–(g). From the Table 7.4 it was quite evident that the consecutive oxidation and reduction processes of GOQDs-en and GOQDs-en-Co$_3$O$_4$NPs exhibited consistent reversibility in PL emission intensity upto three consecutive redox cycles. Therefore this system could probably be very well
suited for reversible on/off fluorescence switching optoelectronic device applications based on functionalized carbon nanomaterial-based hybrid quantum systems.

7.5.3 Mechanistic Insight

The mechanism of reduction and functionalization of GOQDs by ethylene diamine via ring opening of epoxy groups had already been reported earlier. The mechanism for the reduction of GOQDs by ethylene diamine was proposed to occur via reaction of the diamine with epoxy groups on GOQDs by a ring opening addition reaction; the driving force for the reaction being the strain on the three-membered epoxy ring which was always known to have a tendency to open up. Further, some of the amine groups would also react with the carboxylic acid groups on the GOQDs surface to form covalent amide (–CONH–) linkages.

Scheme 7.2 (A) The schematic representation of the reduction of GOQDs by ethylene diamine and covalent functionalization to form –NHR linkages on GOQDs. (B) Schematic representation of
immobilization of Co$^{2+}$ ions by coordination to ethylene diamine within the layers of GOQDs-en and in situ formation of Co$_3$O$_4$NPs.

The schematic representation of the reduction of GOQDs by ethylene diamine and covalent functionalization to form $\text{--NHR}$ linkages is shown in Scheme 7.2 (A). Schematic representation of immobilization of Co$^{2+}$ ions by coordination to ethylene diamine both within the layers and on the surface of GOQDs-en and in situ formation of Co$_3$O$_4$ NPs is shown in Scheme 7.2 (B). The mechanism for formation of Co$_3$O$_4$NPs was proposed to be the coordination between ethylene diamine attached to the GOQDs and Co$^{2+}$ ions in solution to form a stable complex which was proposed to cause the immobilization of Co$^{2+}$ within the graphene layers of GOQDs-en. Further addition of H$_2$O$_2$ led to the formation of Co$_3$O$_4$NPs with the liberation of ammonia due to the oxidizing nature of H$_2$O$_2$ thereby indicating the successful breaking of Co–N bond to form Co$_3$O$_4$NPs. The procedure adopted for formation of Co$_3$O$_4$NPs had already been reported and had been employed in our system with slight modifications.\textsuperscript{277}

\textbf{7.6 Conclusion}

In this work we demonstrated the design of a novel carbon-based hybrid nanomaterial i.e., GOQDs-en-Co$_3$O$_4$NPs derived from ethylene diamine mediated reduced graphene oxide quantum dots and inorganic cobalt oxide nanoparticles. From experimental evidences discussed, the process can be summarized as successful oxidation, exfoliation of graphene platelet nanosheets into GOQDs by introducing different oxygen functionalities into their surface; successful reduction and functionalization of GOQDs by ethylene diamine via ring opening of epoxy groups on the surface of the different layers of GOQDs by formation of $\text{--NH}$ linkages to form
GOQDs-en and finally immobilization of Co$^{2+}$ ions by coordination to ethylene diamine within the layers and on the surface of GOQDs-en via in situ formation of Co$_3$O$_4$NPs. The prepared samples were subjected to extensive stepwise and systematic characterization via different experimental techniques to demonstrate the successful formation of the samples. An interesting property of the prepared samples was their photoluminescence. The photoluminescence intensity of the GOQDs was found to be enhanced upon reduction and functionalization with ethylene diamine and was found to enhance further upon in situ formation of Co$_3$O$_4$NPs via coordination of en with Co$^{3+}$ ions in solution. The re-reduction of GOQDs-en-Co$_3$O$_4$NPs with en resulted in a decrease of PL intensity whereas further re-oxidation with H$_2$O$_2$ and Co$^{3+}$ ions caused an enhancement in the PL intensity due to reformation of Co$_3$O$_4$NPs and so on. This reversible on/off PL switching property of the system was found to be consistent as studied upto three consecutive oxidation-reduction cycles. Therefore, the system designed was an organic-inorganic hybrid composite nanomaterial with interesting PL properties and could potentially serve as an ideal candidate for application in optoelectronic devices as a reversible on/off photoluminescence switch.