



# Photoluminescence Quenching in Metal Ion ( $\text{Cu}^{2+}$ , $\text{Co}^{2+}$ ) Interacted Graphene Quantum Dots

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Graphene quantum dots (GQD) are nanosized fragments of graphene with finite band gap. Thus, GQDs show excellent photoluminescence (PL) and also possess good electrochemical properties. In the present study, we synthesized GQDs via hydrothermal (HT) method using Graphene oxide as prepared from improved Hummer's method as a precursor with several modifications. The effect of the variation in the photoluminescence and electrochemical properties of the as-prepared GQDs were studied. Average particle size of the as-synthesized GQDs was roughly 30 nm and produced blue PL on excitation with a wavelength of 365 nm. On reacting the GQDs with Cupric Nitrate and Cobalt Nitrate in separate batches, a significant decrease in the intensity of PL was observed. This quenching of PL of GQDs has been utilized in the qualitative estimation of Metal ion ( $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$ ) species in aqueous media.

## 1. Introduction

Graphene Quantum Dots (GQDs) are zero-dimensional graphene fragments such as the movement of the exciton is confined in all three spatial directions. Unlike graphene, GQDs possess a finite band gap which along with exciton confinement leads to photoluminescence. The infinite Bohr radius of graphene able researchers with the ability to tune the photoluminescence of GQDs by varying its size. GQDs are thus widely used for a variety of application few of which are photovoltaic devices,<sup>[1]</sup> organic light-emitting diodes,<sup>[2]</sup> fuel cells<sup>[3]</sup> and drug delivery systems<sup>[4]</sup> etc.

Since its discovery, GQDs have found widespread applications as sensors.<sup>[5]</sup> The sensing ability of GQDs ranges from biomolecules to oxidants, and from toxins to explosives. The mode of sensing studied with GQDs ranges from the electrochemical sensor, photo-luminescent/fluorescent sensors, colorimetric sensors and hybrid sensors. GQDs have shown immense potential in electrochemical sensing of biomolecules, like DNA,<sup>[6]</sup> proteins,<sup>[7]</sup> Amino acids,<sup>[8]</sup> Uric Acid,<sup>[9]</sup> Glucose<sup>[10]</sup> and even detection of the virus<sup>[11]</sup> have been reported. This

shows promising potential of Graphene Quantum Dots for chemical sensing applications.

Heavy metals (or Transition Metals) are among the most toxic pollutants found in water. Exposure to metal ions has been related to various disorders in humans which include respiratory problem, carcinogenicity, nervous system failure and poisoning. However, few are also essential for healthy functioning of human body. Copper and Cobalt are two of those metals. Copper is essential in forming red blood cells and to maintain healthy nerve cells and immune system. It also assists in the formation of collagen found in bones and connective tissue. The adverse effects of excessive copper intake include vomiting, diarrhea, stomach cramps, and nausea. It has also been associated with liver damage

and kidney disease. Cobalt is another essential metal which is an important component of vitamin B<sub>12</sub>. These metals are a common occurrence in environment and water and with an increase in applications of nanoparticles makes this problem even more severe.<sup>[12,13]</sup> Various methods developed to sense these elements involve primarily the use of complex organic molecules, or peptides via electrochemical determination.<sup>[14–17]</sup> Organic ligands have also been used for fluorometric determination  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  ions.<sup>[18,19]</sup> Although these sensors being efficient, usually involve the use of molecules which are not readily available and their synthesis makes them cost inefficient. Here, we demonstrated how PL of GQDs can be utilized in the possible qualitative determination of metal ions using  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  ions. Preparation of these GQDs are facile and offers very fast qualitative detection.

## 2. Experimental Section

Graphite was procured from Sigma Aldrich. Sulphuric Acid, Nitric Acid, Phosphoric acid, Hydrogen peroxide, Hydrochloric acid and Sodium hydroxide were from Finar Chemicals and used without further purification.

In a typical synthesis procedure (scheme represented in **Figure 1**) Graphene oxide was prepared using Improved Hummer's method.<sup>[20]</sup> Further, as prepared Graphene Oxide were put in a Teflon-lined autoclave in alkaline medium and reaction was kept for 16 hours at 200 °C which is in accordance to hydrothermal synthesis reported by Pan et al.<sup>[21]</sup> with modifications. Aqueous GQDs thus synthesized were reacted in separate batches with Cupric(II) Nitrate

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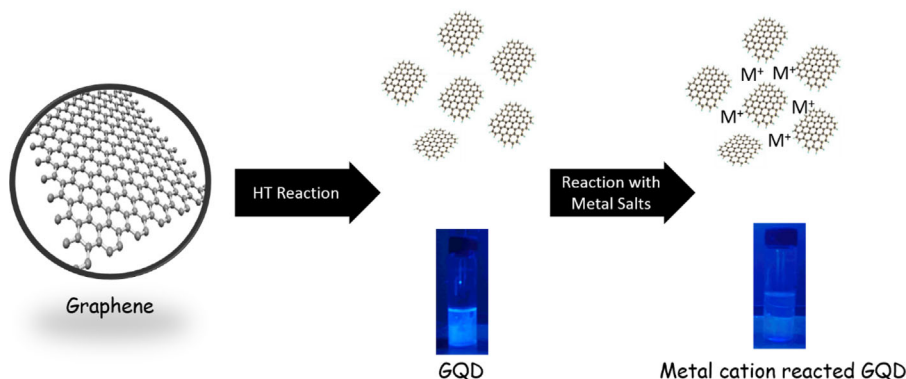


Figure 1. A graphical representation of synthesis procedure.

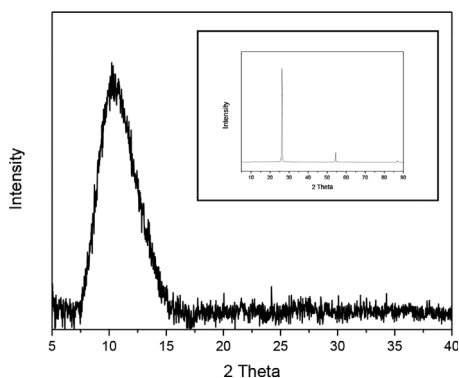


Figure 2. XRD spectrum of Graphene oxide (Inset: XRD Spectrum of Graphite).

and Cobalt(II) Nitrate respectively. GQDs were characterized using Bruker Alpha Eco-ATR FTIR, Analytik Jena Specord S600 UV-Vis Spectrophotometer, and Horiba Fluoromax Spectrofluorometer.

### 3. Results and Discussion

Graphene oxide as synthesized was analyzed using X-ray diffraction. The presence of the characteristic broad peak at

$2\theta$  of 7.5–15 degree corresponding to the (002) plane of graphene oxide (Figure 2) instead of the usual sharp peak at 26 degrees for graphite suggest a synthesis of high purity graphene oxide.

Figure 3(A) represents the FT-IR spectra of Graphite, graphene oxide and GQDs as recorded from  $4000\text{--}600\text{ cm}^{-1}$ . The spectra reveal the presence of oxygen-containing functional groups attached to the all carbon structure. In the present graph, there are no peaks for graphite, which confirms the absence of oxygenated functional groups from the starting material.

In graphene oxide, we observe characteristic peaks corresponding to the  $\text{--OH}$  at  $3200\text{--}3600\text{ cm}^{-1}$ ,  $\text{C=O}$  at  $1670\text{--}1820\text{ cm}^{-1}$  and  $\text{--COC}$  at  $1000\text{--}1300\text{ cm}^{-1}$ , which are the usual defects 2-dimensional sheet of graphene oxide. In GQDs, we observe only peaks corresponding to the  $\text{--OH}$  at  $3200\text{--}3600\text{ cm}^{-1}$ ,  $\text{C=O}$  ( $1670\text{--}1820\text{ cm}^{-1}$ ) which are indicative of  $\text{--COOH}$  terminating edges of GQDs. These  $\text{--COOH}$  groups further play important role in binding with Co(II) and Cu(II) ions. Figure 3(B) shows the fingerprint region of IR for as prepared, Co interacted GQDs and Cu interacted GQDs. It clearly shows the presence of Co-O at  $610$  and  $627\text{ cm}^{-1}$  and Cu-O-H deformation vibrations at  $685\text{ cm}^{-1}$  (sh, br) and  $875\text{ cm}^{-1}$  (w, br),<sup>[22]</sup> which are absent in as prepared GQD. This indicates the successful binding of GQDs to  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  ions through oxo linkage.

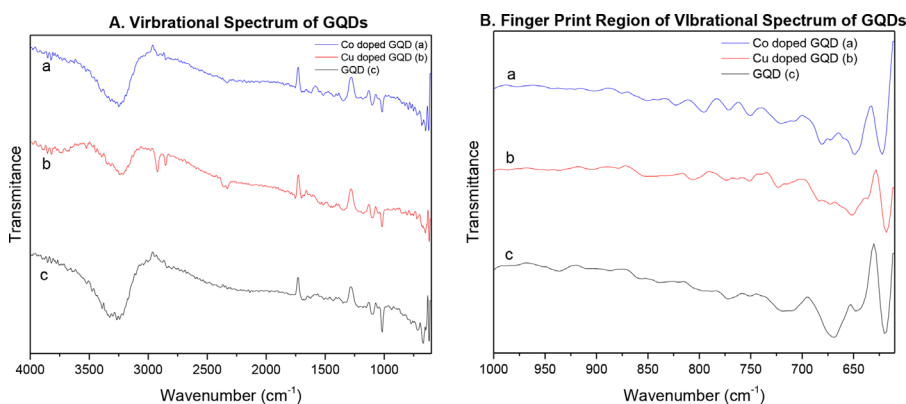
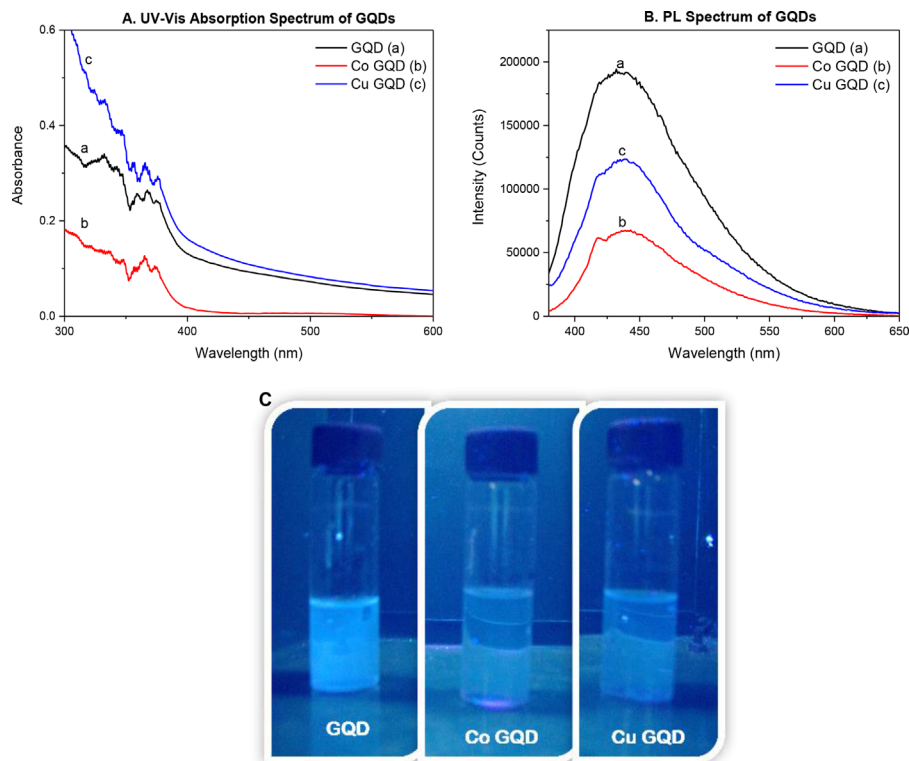


Figure 3. A) FTIR spectra of GQDs, Co interacted GQDs and Cu interacted GQDs, B) Fingerprint region of GQDs, Co(II) interacted GQD and Cu(II) interacted GQD.



**Figure 4.** A) UV-Vis spectra of GQD, Co (II) interacted GQD and Cu(II) interacted GQD, (B) PL spectra of GQD,  $\text{Co}^{2+}$  interacted GQD and  $\text{Cu}^{2+}$  interacted GQD at 365 nm excitation, (C) GQD,  $\text{Co}^{2+}$  interacted GQD and  $\text{Cu}^{2+}$  interacted GQD under 365 nm irradiation (left and right respectively).

As discussed earlier, Luminescence is a very important property for quantum dots. GQDs prepared herewith showed typical blue luminescence. **Figure 4(A)** shows the UV-Vis absorption spectrum of GQDs, Co and Cu interacted GQDs, absorbs at 365 nm which was used as excitation wavelength for PL studies. **Figure 4(B)**, shows the PL spectra of as prepared GQDs, and  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  interacted GQDs.

It is evident that luminescence of GQDs has been drastically quenched due to interaction with metal ions. The apparent loss of intensity can be well visualized from **Figure 4(C)** which compares luminescence of GQDs, Co-GQDs and Cu-GQDs under irradiation of 365 nm. It is inferred that the long-range interaction of GQDs around metal ions relieves the excitonic barrier which is responsible for this observed photoluminescence quenching. A schematic representation of which was earlier presented (**Figure 1**). The extent of photoluminescence quenching being different for both the metal ions are indicative that the selective determination of metal ions may be possible after careful optimization.

#### 4. Conclusions

GQDs are well synthesized via Hydrothermal cutting of GO sheets and this reduction in size leads to the excitonic entrapment within the GQDs structure leading to its semiconducting non-zero band gap and subsequent photoluminescence. Metal ion interacts with GQD core via oxo-linkage with dangling oxygens at the edge of

GQDs. The quenching of PL observed in  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  interacted GQDs is due to long range conjugation around metal ions which relax excitonic barrier. This PL quenching is well utilized in fast qualitative sensing of metal ions ( $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$ ) present in the aqueous medium. The reported PL quenching of GQDs in presence of metal ions can be further extended towards their quantitative determination.

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#### Keywords

graphene quantum dots, photoluminescence quenching, qualitative determination

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