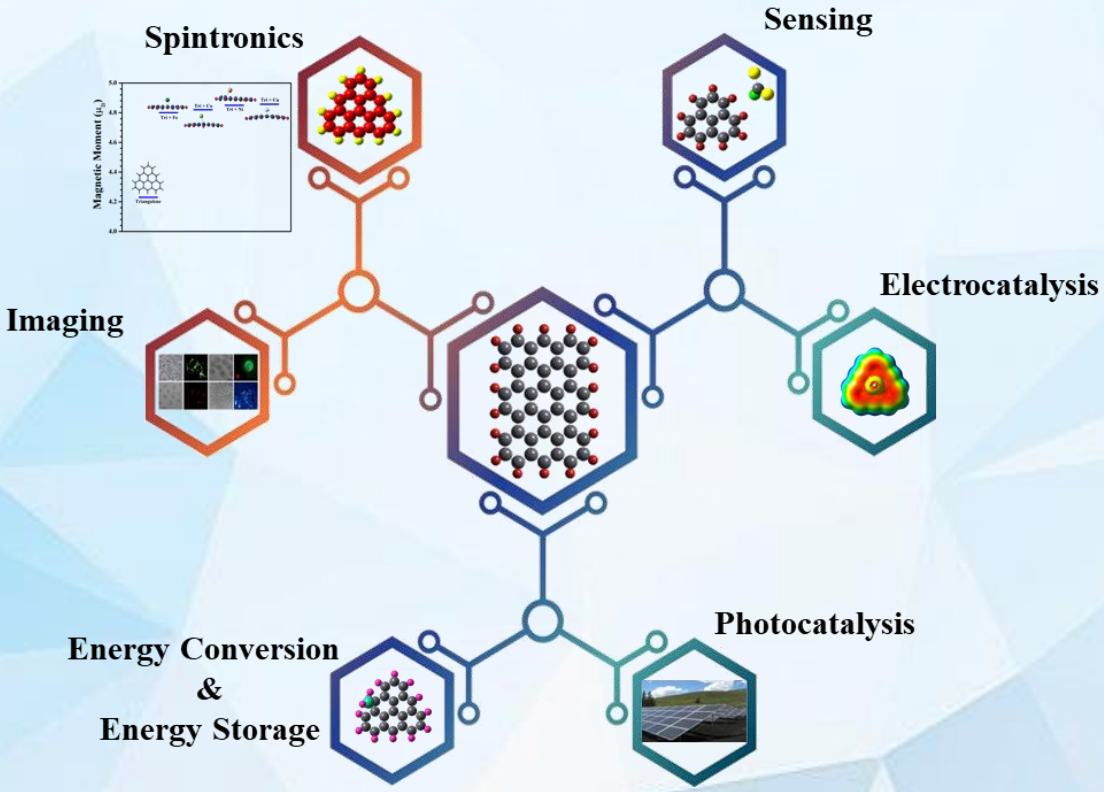
Chapter 7

Summary and Future Scope



The present thesis is structured in the following way. The ***Chapter 1*** unveils the pathway of carbon family including groundwork for novel family member "graphene quantum dots (GQDs)" along with their unique chemical and physical properties on account of edge and quantum confinement effects. The experimental and theoretical ongoing scientific advancement in the field of GQDs are underlined. A handful of fabrication approaches and important properties are acknowledged. Despite the fact that GQDs comprise many advantages and promising applications, GQDs display some limitations constricting its utilization which will conquer by functionalization. The variation in the properties of GQDs using functionalization (doping with heteroatoms, oxidation, and surface/edge functionalization) accompanied by energy, optical and medical applications is also presented. Nevertheless, understanding of GQDs will assist in predicting the future evolution trend and its challenges and opportunities.

The first principles based density functional theory (DFT) presented in ***Chapter 2*** has been the computational methodology for the evaluation of new properties of GQDs for different applications. In recent past, DFT emerged as a significant approach due to developed computational facilities, numerical methods and succession of several new exchange-correlation functionals. Origin and formalism of DFT starting with the many body problem to Kohn-Sham approach along with its implementation in Gaussian09 software package is addressed. Exchange-correlation accompanying basis sets, linear response theory and time-dependent density functional theory (TD-DFT) are briefly illustrated. Subsequently, applications of quantum chemical methods like geometry optimization, frequency, molecular orbitals, dipole moment and UV spectra calculations are discussed.

Chapter 3 presents the geometrical, electronic, vibrational and magnetic properties of triangulene, a model for GQD. Being the smallest triplet-ground-state polybenzoid comprising even number of carbon atoms, it Kekulé structure is unattainable resulting two unpaired electrons as a residue. From DFT calculations, it is found that the triplet ferromagnetic state (FM) is more stable as compared to singlet anti-ferromagnetic state (FM). The existence of spins (due to two unpaired electrons) leads to the investigation of magnetic properties of triangulene making its utilization in electronics, quantum computing, quantum information processing and spintronics. The effect of magnetic elements iron (Fe), cobalt (Co), nickel (Ni) and copper (Cu) was also studied and found that the magnetic moment (M) enhances from 4.23 μ_B to 4.857 μ_B with Cu

being the highest (Fig. 7.1). The results of present work propose that inclusion of magnetic elements in GQDs can find its application in information readout devices and spintronics.

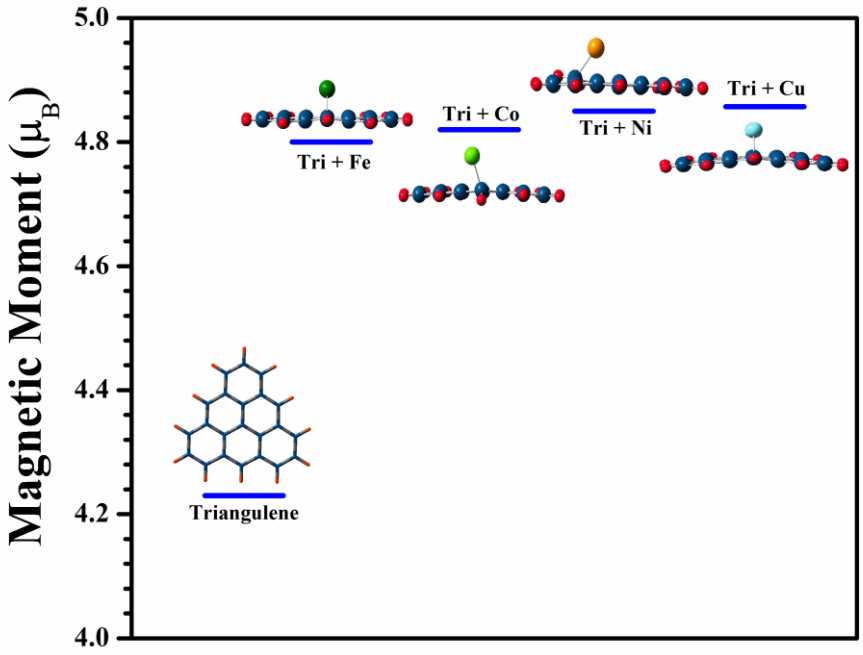


Figure 7.1: Magnetic moment of pristine and iron, cobalt, nickel, copper doped triangulene depicting their superiority.

In the ever-expanding need of energy capitals, production of hydrogen has gained considerable interest in scientific society. ***Chapter 4*** presents two fold studies (i) hydrogen evolution reaction (HER) activity of triangulene through adsorption mechanism and electronic properties calculation and (ii) investigation of platinum adsorbed triangulene for the applications in hydrogen storage. In the former study, triangulene gives superior HER activity with -0.264 eV of adsorption energy as compared to other quantum dots. The latter study presents adsorption of hydrogen (H_2) on platinum adsorbed triangulene (Pt+tri) considering three sites (a) hollow, (b) top (c) and bridge. The schematic of adsorption energy trend of H_2 over Pt decorated triangulene is presented in Fig. 7.2. However, Pt atom at hollow site is most stable in comparison with other two. Present results display that H_2 disjoints intuitively over all hollow, top and bridge sites of Pt+tri introducing D-mode. These elementary insights of adsorption mechanism in addition to

investigation of electronic properties will turn out to be essential for additional exploration of spillover mechanism with fabrication of efficient GQDs for H_2 storage utilization.

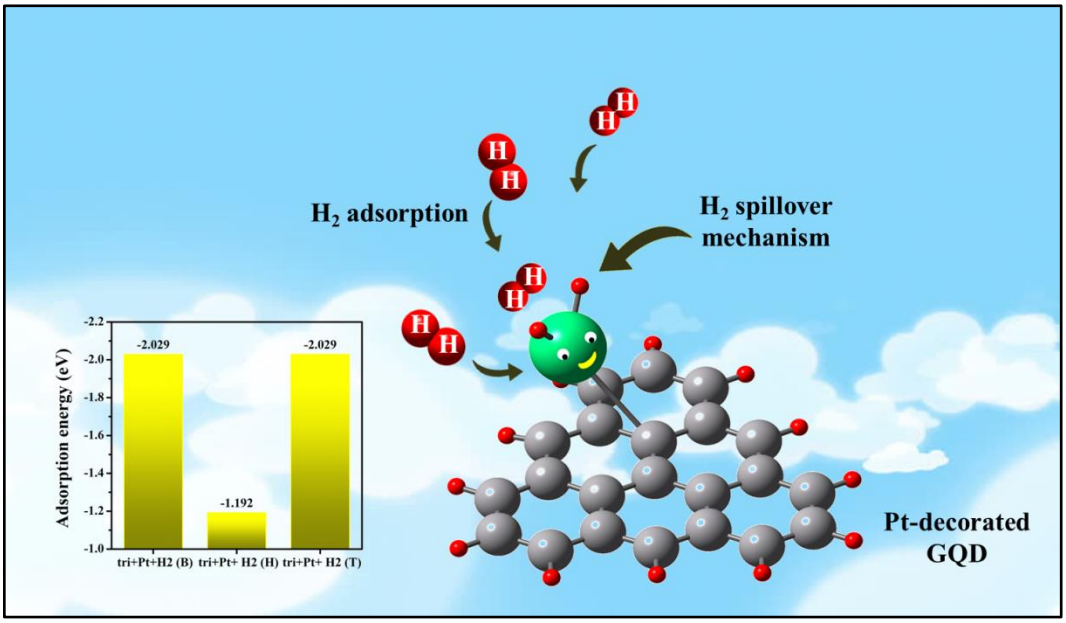


Figure 7.2: Schematic of adsorption energy trend of H_2 over Pt decorated triangulene.

Chapter 5 contains results of the DFT calculation on influence of adatoms such as nitrogen, boron and phosphorus over carboxyl group functionalized GQD on edges (COOH-GQD) for their possible applications in new, non-hazardous and efficient quantum dot solar cells (QDSCs). Figure 7.3 represents the schematic for photo-induced transmission of electrons from COOH-GQD behaving as a donor to the TiO_2 surface behaving as an acceptor. Modification in electron properties by external adatoms are scrutinized through highest occupied molecular orbitals (HOMO), lowest unoccupied molecular orbitals (LUMO), and energy gaps (E_g). Adsorption mechanism, Mulliken charge transfer along with molecular electrostatic potential (MESP) are also demonstrated in order to examine injection of electrons and charge separation in pristine COOH-GQD and N/B/P incorporated COOH-GQD. The absorption spectra of GQDs present wide visible range spectrum which is advantageous to yield solar light. For the utilization of GQDs in QDSC, solar cell parameters like open circuit voltage, fill factor, short circuit current density and power conversion efficiency are evaluated. The present work provides the results on

the increment of η in doped GQDs by 22–30%. The inclusion of phosphorus presents maximum η attributed to its superiority in electron donation as compared to others leading to more electron injection on TiO_2 surface. The present chapter presents that the GQD based sensitizers can be potential contestants for QDSCs application.

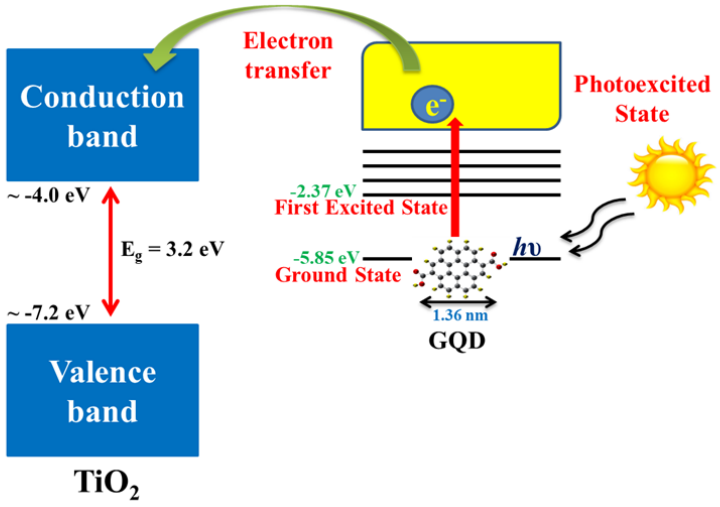


Figure 7.3: Schematic of photo-induced injection of electrons from COOH-GQD into the surface of TiO_2.

Chapter 6 presents the detection and sensing of an organic compound melamine in food products because of its dangerous consequences in humans and animals. The present chapter carries the results of adsorption mechanism of melamine over two kinds of GQDs: (i) oxygen doped COOH-GQD denoted as (O-GQD) and sulphur doped COOH-GQD denoted as (S-GQD) and (ii) epoxy, hydroxyl and carboxyl group functionalized GQD (*f*-GQD). The schematic represented of both models are presented in Fig. 7.4. In addition to DFT calculations, a constructive vibrational spectroscopic method namely surface enhanced Raman scattering (SERS) is chosen to check the sensing of melamine molecule over these GQDs. The E_{ad} of -1.18 and -0.15 eV is evaluated for adsorption of melamine over O-GQD and S-GQD. The intensity of characteristic peak obtained at 688 cm^{-1} increases to 348.4% and 48% in melamine SERS over O-GQD and S-GQD respectively. To evaluate the efficiency of our model, chemical enhancement factor (*EF*) is calculated which is 4.51 (O-GQD) and 1.48 (S-GQD). These values of EF are superior to melamine-silver model. The theoretical studies on SERS of melamine over

doped GQDs propose that the oxygen is better compared to sulphur for SERS. On the other hand, underlying mechanism of melamine adsorption with pristine GQD and *f*-GQD with three different sites are studied to compare the results. The adsorption energy -0.16 eV increases to -0.53 eV at hollow site with melamine adsorption on *f*-GQD. The *EF* value of 39.89 is obtained for peak 736 cm^{-1} which is even higher as compared to melamine over doped GQDs and silver substrate. Accordingly, our results depict that GQDs are potential and efficient surfaces for melamine detection.

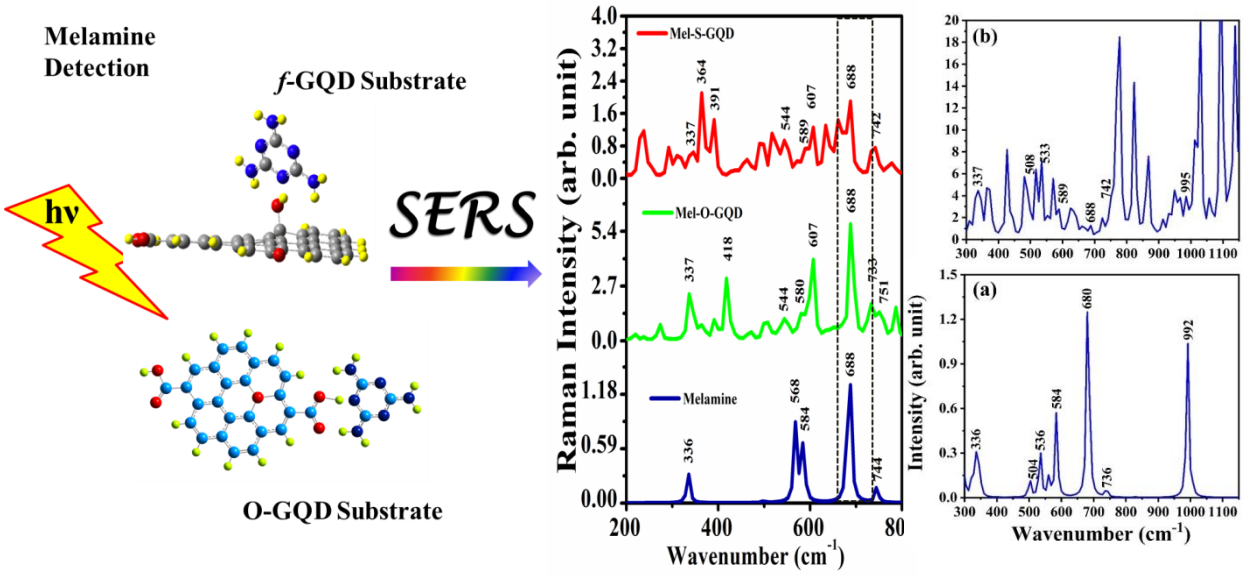


Figure 7.4: Schematic of melamine adsorbed on O-GQD and f-GQD along with their SERS.

Future Scope

Graphene quantum dots have been actively blooming as a breakthrough for applications in diverse fields like photonics, composites, energy, and electronics. The research and development on GQDs are nevertheless at starting point and some challenges are yet to be settled. Besides different significant benefits of GQDs with promising characteristics, further research is required to fulfill their utilization in applications. In the present thesis, we have studied properties of various graphene quantum dots for their possible application in various sectors like spintronics, HER and hydrogen storage, quantum dot solar cell devices and as a potential substrate in SERS.

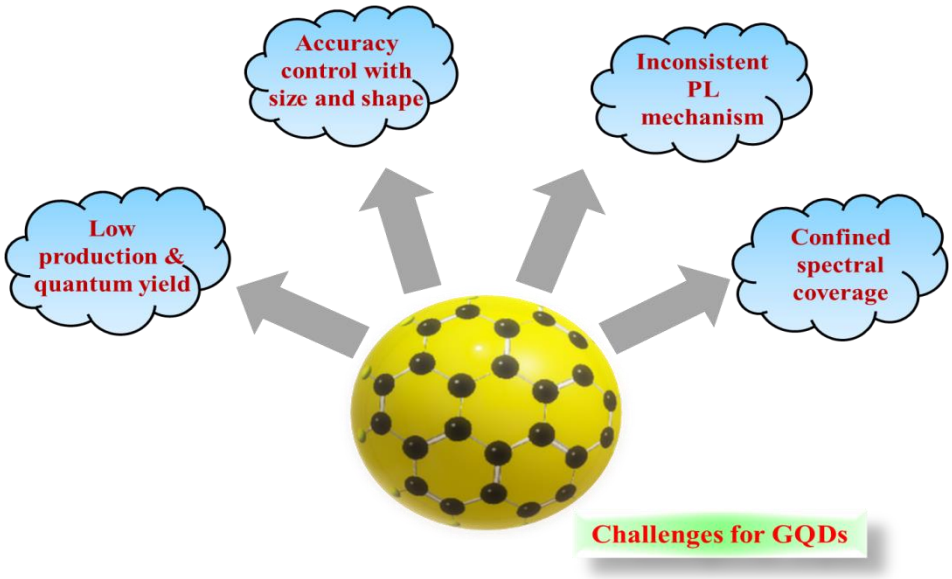


Figure 7.5: Challenges for GQDs that are needed to be addressed.

The production and quantum yield for GQDs are relatively low as compared to conventional semiconductor quantum dots that are needed to be addressed further. Additionally, the properties of GQDs are size and shape dependent, therefore accuracy in these intrinsic properties are needed. Combined theoretical and experimental studies are solution for GQDs. Theoretical studies can also be done to better understand the inconsistent photoluminescence (PL) as there are various methods for the fabrication of GQDs. The confined spectrum of GQDs is restricting their utilization in optoelectronic devices. The enlargement of spectrum can be done through functionalization of GQDs by various means. In particular, there is always a room for improvement and considering GQDs based research which is mushrooming day-by-day for their potential applications in almost all directions.

"A scientist in his laboratory is not a mere technician: he is also a child confronting natural phenomena that impress him as though they were fairy tales."

By Marie Skłodowska Curie