Structural, Electronic and Vibrational Properties of Functionalized Graphene Quantum Dots Using Density Functional Theory

A THESIS

SUMMARY

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BY

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Summary

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) is more stable than singlet (anti-ferromagnetic) state. 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. 1). The results of present work propose that inclusion of magnetic elements in GQDs can find its application in information readout devices and spintronics.

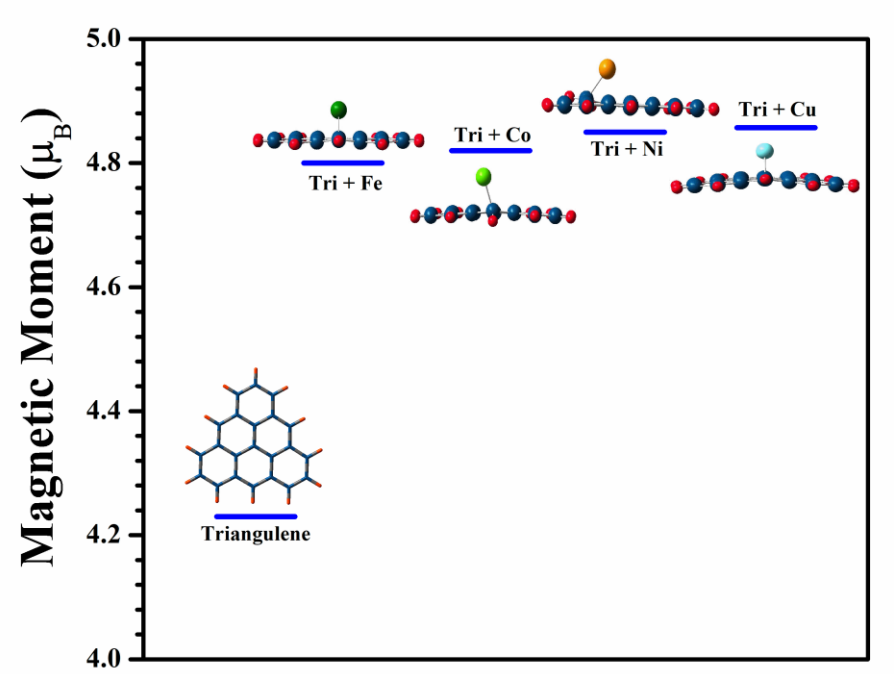

Figure 1: Magnetic moment of pristine and Fe, Co, Ni, Cu doped triangulene depicting their superiority.

In the ever-expanding need of energy resources, hydrogen production has gained much interest in the 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 adsorption energy of -0.264 eV as compared to other quantum dots. The latter study presents adsorption of hydrogen molecule (H_2) over platinum decorated triangulene (Pt+tri) considering three different 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. 2. However, platinum atom is more stable at hollow site 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 be essential for further studying spillover mechanism and synthesis of high-performance GQD for H_2 storage applications.

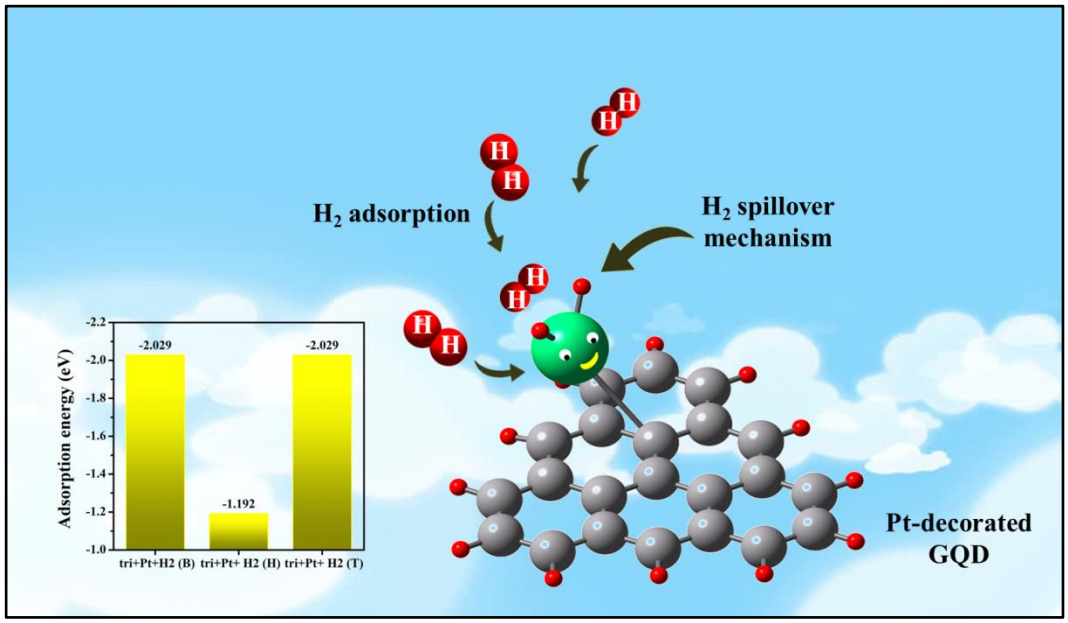

Figure 2: Schematic of adsorption energy trend of H_2 over Pt decorated triangulene.

Chapter 5 contains results of the DFT calculation on influence of adatoms nitrogen, boron and phosphorus over edge functionalized GQD with carboxyl group (COOH-GQD) for their possible applications in new, non-hazardous and efficient quantum dot solar cells (QDSCs). Figure 3 represents the schematic for photo-induced transmission of electrons from donor COOH-GQD to the acceptor TiO_2 surface. The 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 electron injection and charge separation in pristine and doped COOH-GQD. The absorption spectra of GQDs present broad spectrum in the visible range which is advantageous to yield solar light. For the utilization of GQDs in QDSC, the solar cell parameters like open circuit voltage (V_{oc}), Fill factor (FF), short circuit current density (J_{sc}) and efficiency (η) 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.

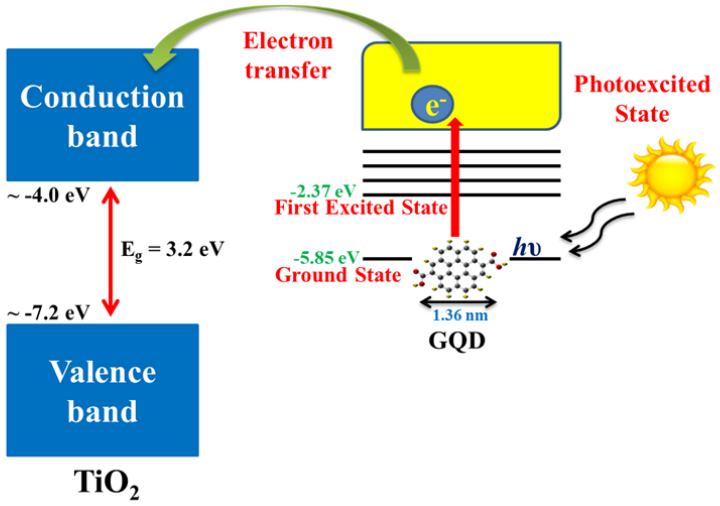

Figure 3: Schematic of photo-induced electron injection from a COOH-GQD into a TiO_2 surface.

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 and sulphur doped COOH-GQD (O-GQD and S-GQD) and (ii) epoxy, hydroxyl and carboxyl group functionalized GQD (*f*-GQD). The schematic represented of both models are presented in Fig. 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 melamine on O-GQD and S-GQD. The intensity of characteristic peak obtained at 688 cm^{-1} increases by 348.4% and 48% in SERS of melamine 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.

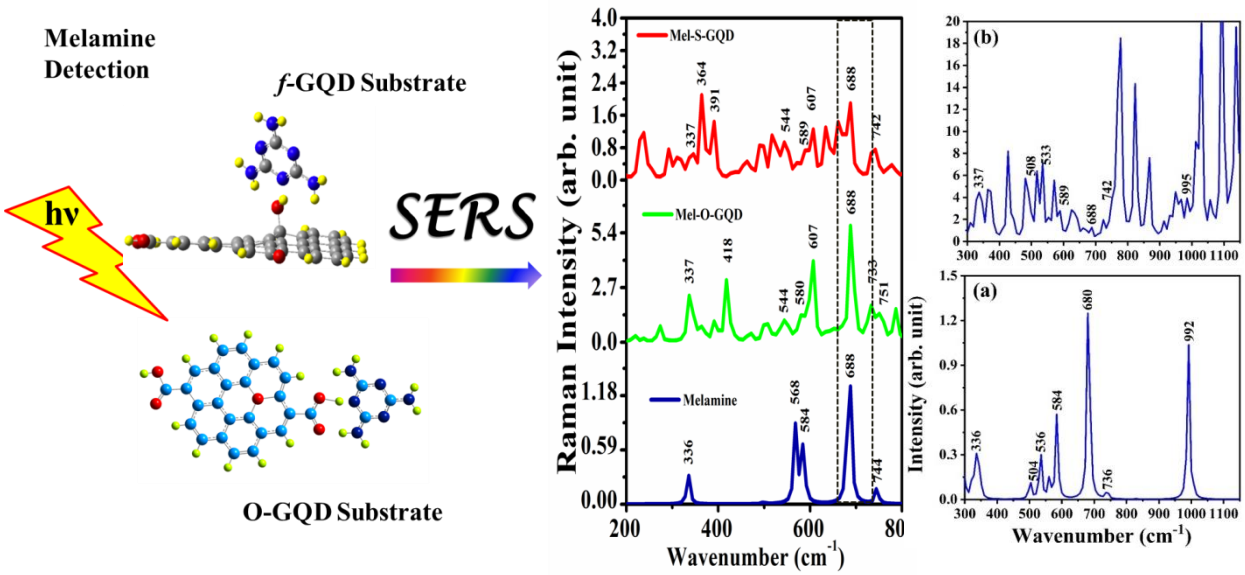

Figure 4: Schematic of melamine over O-GQD and f-GQD along with their SERS.

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, structural, electronic and vibrational properties of melamine over both 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 when melamine is adsorbed over *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 the GQDs are potential and efficient platforms for the detection of melamine molecule.

"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