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

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Introduction

A breakthrough in materials science and engineering realm is taking place as researchers find techniques to design and characterize materials at the nanometre (nm) scale. Novel materials with remarkable electrical, optical, magnetic and mechanical properties are rapidly being developed for their use in information technology, bio-engineering, energy and environmental applications. Graphene, since its discovery, has been unarguably evolving as one of the most promising nanomaterials. In last few years, graphene a flat monolayer of carbon atoms with compact honeycomb lattice and foundation for all carbon allotropes has become an important material for exploration due to its intriguing physical properties, such as quantum electron transport [1-2], tunable band gap [3], high carrier mobility [1-2,4-5], high elastic behaviour [6] and excellent electrochemical properties [7]. The aforementioned properties make it a 'miracle material' for nanoelectronics, photodetectors, composites and coatings, membranes, batteries, super capacitors, storing wind and solar power, biomedical and sensors [8-9]. The noteworthy shortcomings of graphene comprise poor dispersion in solvents and aggregation and zero bandgap. One constructive way to vanquish this drawback is to reduce graphene into nm-scale-pieces, termed as graphene quantum dots (GQDs), opening of band as a consequence [10]. A quantum dot is a nanometre-sized semiconducting object, where excitons are confined in all three dimensions. The new characteristics emerging from edge effects and quantum confinement subsequent to the conversion of two-dimensional (2D) graphene onto GQDs have gained enormous attention in several domains, like physics, chemistry, biology and materials. GQDs that typically have lateral size beneath 100 nm have been technologically advanced in recent years [9,11-12]. Precisely, ideal GQDs consists only carbon atoms with single atomic layer. However, practically, most prepared GQDs comprise oxygen and hydrogen with many atomic layers (size below 10 nm) [13-14]. Due to quantum confinement and edge effects, their bandgap varies from 0 to 6 eV through different size and surface functionalization [15-18]. In

comparison with carbon dots (CDs), a new family member of carbon family "GQDs", acquire incredible chemical and physical properties, for instance large surface area, high surface-to-volume ratio and superior surface grafting through π-π arrangement. GQDs not only achieve intriguing characteristics of graphene [19-22], but also outperform graphene regarding its solubility and broad fluorescence [23-24]. Compared to conventional quantum dots (QDs) such as CdS and CdTe, GQDs exhibit many advantages like low toxicity, chemical inertness, solubility, functionality, crystallinity, biocompatibility and better resistance to photo bleaching [25]. The molecule like character of GQDs makes them easier to handle compared to colloidal QDs. Their electronic, photonic and chemical properties can be altered adequately through chemical doping which is broadly used in the field of carbon nanomaterials. To the best of our knowledge very little work has been done on the electronic and dynamical properties of GQDs particularly for the functionalized systems [26-28]. The structure of the edge-state spectrum and magnetic response of GQDs is strongly dependent on the geometric shape of clusters. Researchers have reported experimental and theoretical studies of GQDs exploring their remarkable promise for future applications. Doping GQDs with heteroatoms provide an attractive means of tuning their intrinsic properties and scrutinizing new phenomena for advanced device applications. White light emission is obtained by combining GQDs with ZnO and other emissive materials in a multilayer light-emitting diode [29]. Yamijala *et al.* have performed a detailed study on the structural stability, electronic, magnetic and optical properties of rectangular GQDs as a function of their size using first-principles calculations based on density functional theory (DFT) [30]. Using DFT, Mahasin *et al.* have shown that the photoluminescence of GQDs can be fine-tuned by controlling their size, shape, edge configuration, chemical functionalization, and doping with heteroatoms [31]. The magnetic and optical properties of diamond shaped GQDs have been investigated by varying their sizes with the help of DFT [32]. Li *et al.* have investigated the electronic structure and optical properties of edge-functionalized GQDs utilizing density functional and many-particle perturbation

theories which show functional groups containing a carbon−oxygen double bond (C=O), namely, aldehyde (−CHO), ketone (−$COCH_3$), and carboxyl (−COOH), are more favourable for tailoring the electronic and optical properties of pristine GQDs [33]. A theoretical study of the structural properties of GQDs by means of atomistic tight-binding theory is performed in which same shapes of GQDs can have different band gaps if they have different edge types. Lower values of band gap are observed on rectangular GQDs compared with parallelogram GQDs [17]. Recently, Hasanzadeh *et al.* reported electropolymerization of a low toxic and biocompatible polymer with entitle poly arginine-graphene quantum dots (PARG-GQDs) as a novel strategy for surface modification of glassy carbon (GC) surface and preparation of a new interface for biomedical application [34]. Most recently, a Swiss-UK team of researchers has successfully created a triangulene molecule by manipulating a precursor molecule (from a mixture of dihydrobenzo [cd,mn] pyrene isomers) physically using a scanning probe microscope tip as they provide an ideal system to explore spin excitations within a single molecule making them promising candidates for spintronic applications [35]. Therefore, to utilize GQDs in diverse areas, a thorough analysis of GQDs is critically needed. Additionally, novel approaches to distinguish GQDs with different sizes, shapes, functional groups are needed to obtain uniform properties of GQDs.

Objectives

The goal of the present thesis is to perform comprehensive first principles study based on density functional theory (DFT) of graphene quantum dots and its functionalization and further to provide the knowledge of underlying physics and chemistry behind functional group's interactions with GQDs. With increased activity in their synthesis, growth and integration in technology and consumer products, there has also been increased concern about their biological, optical, electronics and environmental effects. Therefore, as the production and applications of

GQDs continue to increase, it is deemed critically important to understand their effects and to develop new materials. However, the specific objectives of the present work are following:

1. To obtain a better understanding of the graphene quantum dots (GQDs) structure with various size and shapes.

2. To assess the subtle differences in the electronic properties of graphene quantum dots (GQDs) with different edge structures.

3. To obtain electronic structure, electronic density of states and optical properties of GQDs and functionalized GQDs to utilize them in solar cell applications.

4. To investigate the vibrational properties of GQDs to understand the structure-dynamics-property relationship for their possible applications in surface enhanced Raman scattering (SERS).

5. To understand the binding mechanism between GQDs and functional groups to utilize them in hydrogen evolution reaction (HER) and hydrogen storage.

Summary of Research Work

The present thesis is organized in the following manner.

The **Chapter 1** is all about the journey of carbon family along with the introduction of new family member "graphene quantum dots (GQDs)" and access of their unique properties in almost all directions. The current technological progresses in the field of GQDs on experimental and theoretical aspects are highlighted. Several synthesis techniques and their significant properties are addressed. Besides, the properties of GQDs like bandgap and fluorescence relies on their shape and size. However, GQDs exhibit some limitations restricting its applications which will overcome through functionalization. Chapter 1 also introduces modification of GQDs through various functionalization methods such as doping with heteroatoms, oxidation, and surface/edge functionalization together with their employment in energy, biomedical and environmental applications.

Theoretical description of computational methodology used throughout the work is presented in **Chapter 2**. Formalism of DFT by discussing Kohn-Sham equation [36] to its implementation in Gaussian 09 package [37] is discussed. Exchange-correlation along with basis sets is discussed. Time-dependent density functional theory (TD-DFT) is briefly described. Finally, applications of quantum chemical methods like geometry optimization, frequency, molecular orbitals, dipole moment and UV spectra calculations are given in present chapter.

In **chapter 3,** the structural, electronic and magnetic properties of recently synthesized elusive free standing triangulene using density functional theory is systematically studied. Triangulene, which is a type of graphene quantum dot, is a molecule with an even number of electrons and atoms but the structure of molecule is such that it is impossible to pair all these electrons. The spin of these two unpaired electrons have two possible orientations: triplet (ferromagnetic) and singlet (antiferromagnetic) state (Fig.1).

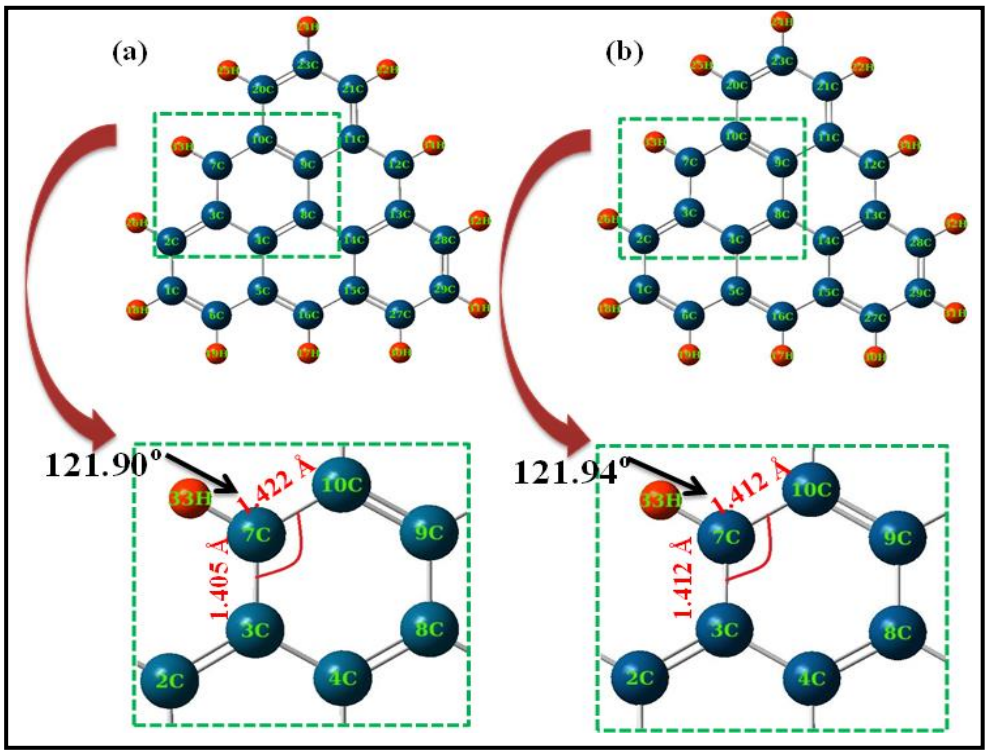

Figure 1: Optimized geometry of free standing triangulene (a) Antiferromagnetic (b) Ferromagnetic. The blue and red ball represents the carbon and hydrogen atoms [38].

The first principles study of free standing triangulene shows that the triplet (ferromagnetic) is more stable than singlet (antiferromagnetic). These elementary studies are technologically compatible as open shell graphene quantum dots could be useful in spintronic and magnetic carbon materials. Further, present study also depicts the influence of magnetic elements Fe, Co, Ni and Cu on triangulene for their applications in spintronics. Our results suggest that the transition metal (TM) doped graphene quantum dot is interesting for information readout devices where the TM-ion spin states can be used to store information.

Chapter 4 comprises investigation of the hydrogen evolution reaction (HER) activity on an open-shell polyaromatic hydrocarbon (PAH), graphene quantum dot "triangulene" using first principles based density functional theory by means of adsorption mechanism and electronic structure calculations. The free energy calculated from the adsorption energy for graphene quantum dot (GQD) later guides us to foresee the best suitable catalyst among quantum dots. Triangulene provides better hydrogen evolution reaction (HER) with hydrogen placed at top site with the adsorption energy as -0.264 eV. Further, platinum decorated triangulene for hydrogen storage is studied. Three different sites on triangulene were considered for platinum atom adsorption namely top site of carbon (C) atom, hollow site of the hexagon carbon ring near triangulene's unpaired electron and bridge site over C-C bond. It was found that the platinum atom is more stable on the hollow site than top and bridge site. We have studied the density of states (DOS), highest orbital molecular orbital (HOMO), lowest unoccupied molecular orbitals (LUMO) and HOMO-LUMO gap of hydrogen molecule adsorbed platinum decorated triangulene. Our results show that the hydrogen molecule (H_2) dissociates instinctively on all three considered sites of platinum decorated triangulene resulting in D-mode. The fundamental understanding of adsorption mechanism along with analyses of electronic properties will be important for further spillover mechanism and synthesis of high-performance GQD for H_2 storage applications.

In **Chapter 5,** in search of novel, non-toxic and high performance materials for the use in quantum dot solar cells (QDSCs), we have investigated the effect of adatoms (nitrogen, boron and phosphorus) on carboxyl edge-functionalized graphene quantum dot (COOH-GQD) through the state-of-the-art first principles calculation based on density functional theory. The HOMO, LUMO and energy gaps are analyzed in order to check the modulation in electronic properties by the foreign atom through hybrid functional B3LYP with 6-31G basis set. Binding mechanism, molecular electrostatic potential (MESP), and charge transfer are investigated to study the electron injection and charge separation in doped/undoped COOH-GQD. Optical properties show broad spectrum in the visible range favorable to harvest solar light. To envisage the application of adatom doped COOH-GQD in QDSC, the solar cell parameters such as open circuit voltage (V_{oc}), Fill factor (FF), short circuit current density (J_{sc}) and efficiency (η) are presented. The efficiency of COOH-GQD increases by 22–30% after the substitutional doping of nitrogen, boron and phosphorus. Maximum efficiency is achieved in case of phosphorus doping due to its more electron donating nature which will inject more electrons in TiO_2 surface. Fig. 2 depicts the photoinduced transfer of electrons from donor GQD to the acceptor TiO_2 surface. Our findings show that these new sensitizers based on GQD are promising candidates for QDSCs applications.

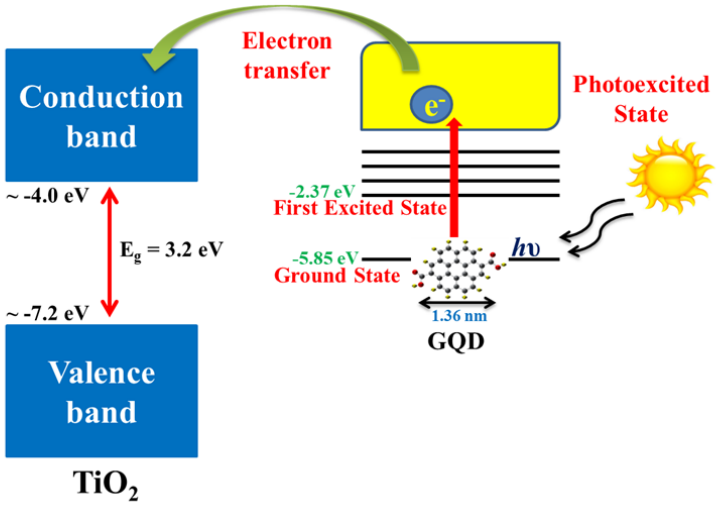

Figure 2: Representation of photoinduced electron injection from a GQD into a TiO_2 surface. An absorbed photon helps an electron from the GQD ground state with energy inside the TiO_2 band gap, into an excited state [39].

The detection and filtration of melamine in food products has become an emergence due to its harmful effect on human. **Chapter 6** consists of investigation of the binding mechanism of melamine over carboxyl group edge functionalized graphene quantum dots doped with oxygen and sulphur atoms (O-GQD and S-GQD). In order to monitor melamine, surface enhanced Raman scattering (SERS) is adopted which is an effective vibrational spectroscopic approach. Electronic and vibrational properties were analysed by means of well adapted density functional theory (DFT). The calculated adsorption energy of melamine over O-GQD and S-GQD is −1.18 eV and −0.15 eV respectively. The characteristic peak of melamine at 688 cm^{-1} is in good agreement with previously reported experimental work and enhances by 348.4% in SERS spectra of Mel-O-GQD and 48% in SERS spectra of Mel-S-GQD. We have calculated the chemical enhancement factor (EF) for melamine over O-GQD and S-GQD and found the enhancement of 4.51 and 1.48 which is greater than melamine silver complexes. Our theoretical studies on SERS of melamine over O-GQD and S-GQD suggest that oxygen is a better candidate for SERS (Fig. 3). Our work demonstrates that the graphene quantum dots are remarkable platforms for the detection of melamine.

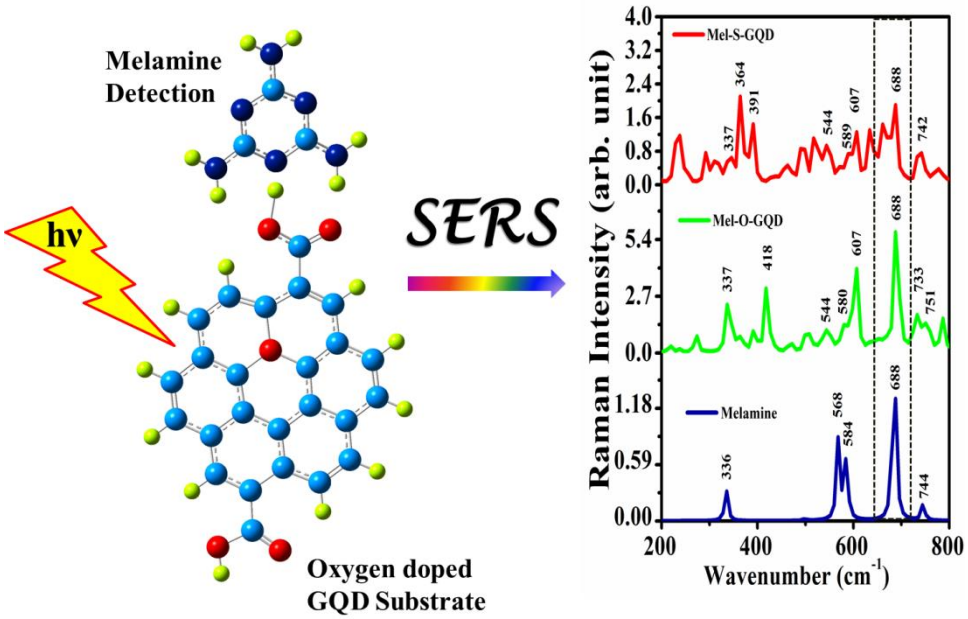

Figure 3: Surface enhance Raman scattering (SERS) mechanism of melamine over carboxyl functionalized GQD [40].

The results of systematic investigation on structural, electronic, vibrational and magnetic properties of various size and shape along with functionalized graphene quantum dots (GQDs) have been summarized in **Chapter 7**. Variation of properties of functionalization compared to their pristine form has been concluded discussing promising applications of GQDs in science and technology followed by a brief discussion on potential future works.

Proposed Content of Thesis

Chapter 1: Introduction

1.1 Brief History of Carbon Family
1.2 From Graphene to Graphene Quantum Dots
1.3 Properties of Graphene Quantum Dots
1.4 Synthesis Methods of Graphene Quantum Dots
1.5 Modification of Graphene Quantum Dots Through Functionalization
1.6 Applications of Graphene Quantum Dots
1.7 Structure of Present Thesis
References

Chapter 2: Brief of Density functional theory

2.1 Many Body Problem
2.2 Traditional Wave Function Based Methods
  2.2.1 Born-Oppenheimer Approximation
  2.2.2 Hartree and Hartree-Fock Approximation
2.3 Density Based Methods
  2.3.1 Thomas-Fermi Model
  2.3.2 Hohenberg-Kohn Theorems
  2.3.3 The Kohn-Sham Approach
2.4 Exchange and Correlation Functional and Basis Set
2.5 Linear Response Theory
2.6 Time-Dependent Density Functional Theory (TD-DFT)
2.7 Applications of Quantum Chemical Methods
References

Chapter 3: Tailoring the Electronic and Magnetic Properties of Peculiar Triplet Ground State Polybenzoid "Triangulene"

3.1. Introduction
3.2. Computational Details
3.3. Results and Discussions
3.4. Conclusions
References

Chapter 4: Hydrogen Adsorption on Pristine and Platinum Decorated Graphene Quantum Dot

4.1. Introduction
4.2. Computational Details
4.3. Results and Discussions
4.4. Conclusions
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List of Publications related to Thesis

1. **Vaishali Sharma**, Narayan Som, Shweta D. Dabhi and Prafulla K. Jha, "Tailoring the Electronic and Magnetic Properties of Peculiar Triplet Ground State Polybenzoid "Triangulene"", *ChemistrySelect*, **3**, 2390-2397, (2018).
2. **Vaishali Sharma** and Prafulla K. Jha, "Enhancement in power conversion efficiency of edge-functionalized graphene quantum dot through adatoms for solar cell applications", *Sol Energy Mater Sol Cells* **200**, 109908, (2019).
3. **Vaishali Sharma**, Narayan N Som, Sharad Babu Pillai, Prafulla K Jha, "Utilization of doped GQDs for ultrasensitive detection of catastrophic melamine: A new SERS platform", *Spectrochim. Acta A* **224**, 117352 (2020).
4. **Vaishali Sharma**, Hardik L. Kagdada, Jinlan Wang and Prafulla K. Jha, "Hydrogen Adsorption on Pristine and Platinum Decorated Graphene Quantum Dot: A First Principle Study", *Int. J. Hydrog. Energy* (Accepted).

Conference Papers

1. **Vaishali Sharma**, Shweta D. Dabhi, Satyam Shinde and Prafulla K. Jha, "Tuning electronic properties of graphene nanoflake polyaromatic hydrocarbon through molecular charge-transfer interactions", AIP Conference Proceedings 1961 (1), 030031, (2018).
2. **Vaishali Sharma**, Som Narayan, Shweta D Dabhi, Satyam Shinde and Prafulla K Jha, "Sensing behavior of a graphene quantum dot phenalenyl towards toxic gases", AIP Conference Proceedings 1942 (1), 050047, (2018).

List of Publications non-related to Thesis

1. **Vaishali Sharma**, Hardik L Kagdada, Prafulla K Jha, Piotr Śpiewak, Krzysztof Jan Kurzydłowski, "Halogenation of SiGe monolayer: Robust change in electronic and thermal transports", *Phys. Chem. Chem. Phys*., (2019). Doi: https://doi.org/10.1039/C9CP03822A
2. Ujjawal Krishnam, **Vaishali Sharma** and Prafulla K. Jha, "The Reynolds number modulated low frequency dynamical modes of aqueous medium embedded spherical

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