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# Tailoring the Electronic and Magnetic Properties of Peculiar Triplet Ground State Polybenzoid "Triangulene"

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In the present work we have studied the structural and electronic properties of recently synthesized elusive free standing triangulene using density functional theory. 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 spins of these two unpaired electrons have two possible orientations: triplet (ferromagnetic) and singlet (antiferromagnetic) state. From the first principles study of free standing triangulene, we found energetically, by koopman's theory of global reactivity descriptors and frequency calculations that triplet (ferromagnetic) is more stable than singlet (antiferromagnetic) which is in good agreement with the previous results. These elementary studies are technologically compatible as open shell graphene quantum dots could be useful in spintronic and magnetic carbon materials. Further we have also studied the influence of magnetic elements Fe, Co, Ni and Cu on triangulene for their applications in spintronics. Our results suggest that the transitional metal (TM) doped graphene quantum dot is interesting for information readout devices where the TM-ion spin states can be used to store information.

## Introduction

Over the past decade, among all the nanomaterials, graphene[1] takes a special place because of its sumptuous properties which results in wide range of applications[2] such as organic semiconductors, chemical sensors, biological engineering, composite materials, energy storage devices, photovoltaic cells, in spintronic and nonlinear optics.[2–3] However, the major problem with the graphene is its direct electronic applications and due to the absence of electronic band gap in it. The band gap in graphene can be opened by controlling the size, such as a nano-ribbon strip and by introduction of other hetero atoms and defects into the graphene moiety.[4] The graphene quantum dots (GQDs) that consist of nanometer-scaled graphene particles with $sp^2$ carbon bonds show great potential in this regard. At this stage most of the applications for GQDs are focused on photoluminescence (PL) related fields energy and display.[5–6] The graphene quantum dots regarded as small piece of graphene are a kind of zero dimensional (0D) material with characteristics derived from both graphene and carbon dots (CDs).[7–8] The GQDs are superior in terms of high photostability, biocompatibility and low toxicity than organic dyes and semiconducting quantum dots (SQDs) due to quantum confinement and edge effects.[7–9] The tiny fragments of graphene sheet results into the nanographene with various polycyclic aromatic hydrocarbon (PAH) units. Therefore the properties of PAHs are closely related to nanographenes.[10–11] These PAHs are made up of fused aromatic rings which lead to the features with almost infinite possibilities that can lead to a rich variety of compounds. There are types of PAHs which acquires a high-spin open-shell radical character in their ground state.[11] For example, phenalenyl[12] contains an odd number of carbon atoms with an odd number of $\pi$ electrons which makes it a radical in its neutral ground state. The extension of benzene rings in a triangular form can lead to several $\pi$-conjugated phenalenyl derivatives such as triangulene (also known as clar's hydrocarbon). Triangulene is the smallest triplet-ground-state polybenzoid, exists as a diradical containing an even number of carbons (22, in fused benzene rings), has been an obscure molecule ever since it was first hypothesized.[13] It is impossible to draw kekulè structure for the whole molecule, two unpaired valence electrons results in every attempt. It is a system containing even number of $\pi$-electrons although the topology of the system means that it is impossible to write a resonance structure in which each $\pi$-electron is paired with one on a neighboring carbon.[14] Due to its extreme reactivity,[13] synthesis and the characterization of free standing triangulene has not been achieved. Recently, triangulene by manipulating a precursor molecule (from a mixture of dihydrobenzo[cd, mn] pyrene isomers) has been successfully created on Cu (111), NaCl (100) and Xe (111).[15] They showed that STM, DFT and AFM calculations confirmed that the triangulene keeps its free molecule properties on the surface and exists in threefold symmetric molecular structure.[15] The expected, aligned spins-the quantum-mechanical property that gives electrons a magnetic orientation due to two unpaired electrons, has inquested triangulene's magnetic properties. This property could make triangulene useful in electronics, applications in quantum computing, quantum information processing and spintronics.[16–17] Though the supportive DFT calculations clearly brings out the free molecule properties of triangulene

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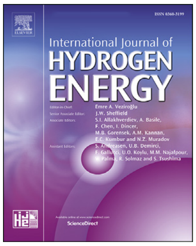

# Hydrogen adsorption on pristine and platinum decorated graphene quantum dot: A first principle study

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## HIGHLIGHTS

- HER activity of graphene quantum dot "triangulene" is studied.
- Triangulene provides better HER with hydrogen adsorption energy of −0.264 eV.
- Site dependent influence of Pt over GQD is evaluated for hydrogen storage.
- Hydrogen on Pt decorated GQD with bridge, hollow and top sites results in D-mode.

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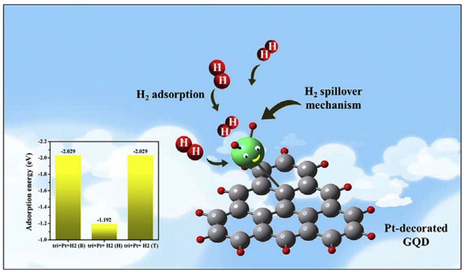
## GRAPHICAL ABSTRACT



## ABSTRACT

In the ever growing demand of future energy resources, hydrogen production reaction has attracted much attention among the scientific community. In this work, we have investigated the hydrogen evolution reaction (HER) activity on an open-shell polyaromatic hydrocarbon (PAH), graphene quantum dot "triangulene" using first principles based density functional theory (DFT) by means of adsorption mechanism and electronic density of states 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 HER with hydrogen placed at top site with the adsorption energy as −0.264 eV. Further, we have studied platinum decorated triangulene for hydrogen storage. 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 is found that the platinum atom is more stable on the hollow site than top and bridge site. We have calculated the density of states (DOS), highest occupied molecular orbitals (HOMO), lowest unoccupied

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# Enhancement in power conversion efficiency of edge-functionalized graphene quantum dot through adatoms for solar cell applications

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ABSTRACT

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 analysed 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 ($\eta$) 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. Our findings show that these new sensitizers based on GQD are promising candidates for QDSCs applications.

## 1. Introduction

To satisfy the world's gigantic need for clean energy, third generation photovoltaic (PV) is becoming the only feasible solution due to its low cost efficiency and electricity generation on earth [1]. The quantum dot solar cells (QDSCs) are arising as a prominent new type of low-cost solar cells due to their extraordinary properties like shape-size tunable gaps, high absorption coefficient etc. [2,3]. Colloidal lead sulfide (PbS), cesium lead iodide ($CsPbI_3$), CdSe and CdTe quantum dots based solar cells are extensively used as QDSCs due to their size-dependent optical properties and potential in surpassing the Shockley-Queisser limit [4–6]. Despite high efficiencies acquired by these QDSCs, they consist of highly toxic metals like lead, cadmium etc. Accordingly low-toxicity, biocompatible and environment-friendly substitutes are in urgent requirement for the fabrication of solar cells. In order to explore significant characteristics of QDSCs, three device compositions were considered: (a) PV effect arising between metal-QD junction, which are named as Schottky junction solar cells, (b) PV effect arising between QD-polymer junction, namely organic solar cells and (c) Quantum dot solar cells (QDSCs) which works on a principle that the photovoltaic (PV) effect takes place among quantum dot combined with metal oxide semiconductor (with wide bandgap) and a redox electrolyte [7–12]. Apparently, they are somehow similar to the dye-sensitized solar cells (DSCs), with the only difference that PV effect takes place between dye-metal oxide semiconductor and redox electrolyte and therefore attracted particular attention for the consideration in solar cells.

Graphene quantum dots (GQDs), a zero dimensional member of the graphene family have been explored greatly due to their unique and significant energy, optoelectronic, light emission and bio-imaging applications [13]. They have attracted so much attention in research society for the utilization in dye sensitized solar cells primarily on account of their nontoxic, highly stable, biocompatible characteristics [13]. Due to the quantum confinement, edge effects, size dependent band gap tailoring and remarkable light harvester they are considered to be well adapted for solar cell applications. For instance, various kinds of carbon dots (CDs) and graphene quantum dots based solar cells have been reported [14]. Up till now, GQDs are used as hole transport layer (HTL) material, semiconductor/GQDs and heterojunction solar cell. Zhang et al. [15] obtained the power conversion efficiency (PCE) of 0.13% for nitrogen doped carbon dots. Recently, Wang et al. [16] designed nitrogen doped carbon dots solar cell with the PCE of 0.79%. Moreover, the power conversion efficiency of QDSCs is yet to be improved. The influence of four heteroatoms on electronic and optical properties of GQDs has been recently investigated [17]. Edge functionalized

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# Utilization of doped GQDs for ultrasensitive detection of catastrophic melamine: A new SERS platform

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ABSTRACT

The detection and filtration of melamine in food products has become an emergence due to its harmful effect on humans. In present work, we have investigated 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 $-1.18$ 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. Our work demonstrates that the graphene quantum dots are remarkable platforms for the detection of melamine.

## 1. Introduction

A decade after the deadly scandal in China resulting in six infant's death and around 3,00,000 illnesses, it is still an unforgettable catastrophe in the world [1]. A national food safety emergency was declared in China due to the illegal addition of a culprit chemical compound “melamine” in infant's milk formula to artificially boost the level of protein [1]. Melamine is nitrogen rich organic compound comprising six nitrogen atoms (67% per mass unit) with the molecular formula, $C_3H_6N_6$ [2]. Melamine is extensively used as an industrial chemical in plastics, fertilizer production, kitchenware, commercial filters, laminates, adhesives, molding compounds, coatings, flame retardants etc. [3–5]. According to America's Food and Drug Administration, the concentration of melamine in milk formula was found to be in high range of 2560 mg/kg. However, the routine tolerable intake for melamine is only 0.63 mg/kg [6]. In addition, inclusion of melamine in petfoods caused deaths of hundreds of dogs and cats in 2007 in USA. The consumption of melamine leads to bladder and kidney stones inducing renal failure in human beings [7,8]. Subsequently, it has become an urgency to detect and control the concentration of melamine in milk products. For the reliable, efficient detection and qualification of melamine, few studies have been reported [9–12].

Up till now, various methods such as liquid chromatography/tandem mass spectrometry [13], mass spectrometry [14] and low temperature plasma (LTP) ionization with tandem mass spectrometry [15] were adapted for the melamine detection. Nevertheless, these traditional methods are tedious which require pretreatment of samples like extraction, pre-concentration and derivatization. Contrarily, Raman spectrum yields “fingerprint-like” information about all chemical constituents in systems with minimal or no preparation of sample and without ruining the samples [16]. However, in spite of the precise and powerful identification of molecules, still the bottlenecks are there for small cross-section molecules which lead in weak Raman signals. Surface enhanced Raman spectroscopy (SERS) has become an attractive area since 1974 [17–19], the first analysis of Raman spectra of pyridine on silver [20]. SERS tremendously improves these weak Raman signals even for single molecule [21,22]. The discovery of SERS leads to the search of active substrate with high sensitivity, reproducibility and uniformity. Traditionally for SERS, number of noble and transition metals (Ag, Au, Cu, Si, Pd) were used as substrates [23,24]. Nonetheless, alternate substrates for SERS are evolving regarding biocompatibility, stability, expenses and eco-friendly characteristics. Graphene [25], a two-dimensional sheet of carbon atoms display incredible Raman scattering properties as compared to noble metals due to its high adsorptivity, chemical stability, biocompatibility along with unique electronic and phonon properties [26]. Graphene-enhanced Raman scattering (GERS), employs graphene

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# Chapter 35
# Trapping Melamine with Pristine and Functionalized Graphene Quantum Dots: DFT and SERS Studies

**Vaishali Sharma, Hardik L. Kagdada, Dheeraj K. Singh and Prafulla K. Jha**

**Abstract** Present study reports structural, electronic, and surface-enhanced Raman spectroscopy (SERS) investigation of melamine on pristine and functionalized graphene quantum dots (f-GQD) using density functional theory. Structural analysis reveals that melamine is strongly adsorbed over f-GQD than pristine GQD through hydroxyl group. Adsorption energy of −0.530 eV shows the physisorption of melamine on f-GQD. HOMO–LUMO gap for pristine melamine is 5.595 eV which reduces to 1.184 eV after adsorption over f-GQD depicting the charge transfer between melamine and f-GQD. The f-GQD plays a vital role in detecting melamine through surface-enhanced Raman spectroscopy (SERS). Three peaks at 584 $\text{cm}^{-1}$, 680 $\text{cm}^{-1}$, and 736 $\text{cm}^{-1}$ are denoted as the characteristic Raman peaks for melamine. A significant shift in Raman spectra of ~10 $\text{cm}^{-1}$ is found after the adsorption of melamine over f-GQD. Interaction between melamine and f-GQD results in the enhancement of Raman intensities of melamine which leads to melamine detection. To evaluate SERS effect, enhancement factor (EF) is evaluated with highly intensified peak at 736 $\text{cm}^{-1}$. The characteristic peak of melamine at 584 $\text{cm}^{-1}$ is increased by 396% when adsorbed over f-GQD. Our study suggests that the f-GQD is an efficient substrate for SERS effect and makes them a potential candidate for detection and sensing of melamine.

## 35.1 Introduction

Melamine is an organic molecule comprising 66% of nitrogen with rest of carbon and hydrogen atoms [1]. Melamine possesses benzene-like structure with three carbon and three nitrogen atoms where $NH_2$ group is attached to carbon atoms. This organic

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# Four-fold enhancement in the thermoelectric power factor of germanium selenide monolayer by adsorption of graphene quantum dot

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ABSTRACT

The present study reports the electronic and thermoelectric properties of graphene quantum dot pyrene adsorbed germanium selenide monolayer using density functional theory calculations. The adsorption energy of 4x4 supercell of germanium selenide monolayer with graphene quantum dot is −0.92 eV suggesting a favorable binding between the germanium selenide monolayer and graphene quantum dot. Our calculations reveal that the Seebeck coefficient for both germanium selenide monolayer and graphene quantum dot adsorbed germanium selenide monolayer (GQD@GeSe monolayer) increases with a decrease in doping level. The value of Seebeck coefficient is highest for zero doping. The incorporation of graphene quantum dot increases the number of charge carriers in germanium selenide monolayer resulting in the amplified electrical conductivity from $0.13 \times 10^{19}$ to $0.52 \times 10^{19}$ $(\Omega ms)^{-1}$ which leads to a very large thermoelectric power factor at room temperature. The power factor is enhanced from $1.17 \times 10^{10}$ to $5.38 \times 10^{10}$ W/mK in germanium selenide. The adsorption of graphene quantum dot with doping level and temperature can be used to generate more output power for the thermoelectric power generation. The present work contributes in understanding the design of germanium selenide monolayer with graphene quantum dot based hybrid structures for thermoelectric devices in the future.

## 1. Introduction

Highly efficient thermoelectric materials will play a key role in future owing to the world's increasing energy consumption and shortage of natural resources. Thermoelectric technology provides an effective direction in converting waste heat into electricity through the Seebeck effect [1]. The combination of semiconducting, electrical and thermal characteristics in thermoelectric materials permits their utilization in cooling and heating [2]. The thermoelectric performance or efficiency of a given material is classified by the dimensionless quantity called figure of merit (ZT), which depends on directly proportional parameters: Seebeck coefficient (S) and electrical conductivity (σ). However, ZT is inversely proportional to the thermal conductivity which further involves two parts: electronic thermal conductivity ($\kappa_e$) and lattice thermal conductivity ($\kappa_l$). High ZT and power factor can be achieved by enhancing the Seebeck coefficient which can be achieved by reducing the dimension of materials. The low dimensional materials lead to increased phonon scattering which reduces the lattice thermal conductivity and improves the ZT [3]. In last few years, researchers have improved the ZT for low dimensional materials including two-dimensional (2D) heterostructures and zero dimensional materials. The thermal conductivity is lower in nanocomposites than their alloys counterparts (with similar chemical composition) [4]. For example, silicon, the ZT value of ~0.01 in the case of bulk silicon enhances to 0.1 (about 100 times) in its nanowire form [5]. This increment is mainly attributed to the reduction of lattice thermal conductivity attained by reducing the dimension of silicon i.e. bringing it to nanowire form from its bulk form. The ZT of ~0.4 at room temperature is found in case of thin silicon membranes [6].

Among new materials under intense scrutiny, 2D materials now-a-days are being extensively explored for thermoelectric applications due to better performance than their bulk counterpart. The chemical functionalization, doping, defect and strain engineering, and formation of heterostructure have shown to significantly affect the thermoelectric properties of 2D materials [7]. Apart from the nanostructuring, doping, creating structural defects

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# Halogenation of SiGe monolayers: robust changes in electronic and thermal transport†

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Phonon and electronic transport of buckled structured SiGe monolayer and halogenated SiGe monolayers ($X_2$–SiGe, X = F, Cl, and Br) are investigated for the first-time using *ab initio* density functional theory (DFT). The phonon calculations reveal complete dynamical stability of SiGe and fluorinated ($F_2$–SiGe) monolayers in contrast to earlier reported works, where a small magnitude of imaginary frequency in SiGe monolayer near the zone centre of the Brillouin zone (BZ) is observed. The phonon calculations of chlorinated and brominated SiGe reveal no dynamical stability even with very high convergence parameters and better computational accuracy. The lower value of lattice thermal conductivity in the case of $F_2$–SiGe is attributed to the strong phonon anharmonic scattering and larger contribution of the three phonon process to anharmonic scattering. The semimetallic nature of the SiGe monolayer turns to semiconducting after halogenation. We have also calculated the electron relaxation time to study their precise thermoelectric parameters. The enhancement of the Seebeck coefficient and reduction in lattice thermal conductivity in the SiGe monolayer is observed after halogenation which results in the improvement of the thermoelectric figure of merit (*ZT*). The room temperature figure of merit, *ZT*, which is 0.112 for the SiGe monolayer, enhances significantly to 0.737 after addition of fluorine atoms. Our study suggests that the halogenation of two-dimensional materials can improve their thermoelectric properties.

## 1. Introduction

Ever since the discovery of graphene,[1] two-dimensional (2D) materials have gained much attention and been studied widely both experimentally and theoretically due to their potential applications in next generation electronics, sensors, energy conversion devices *etc.*[2] Among them, silicon (Si) and germanium (Ge) nanostructured materials are becoming the main pillars in materials science.[3,4] It was shown that Si and Ge have a slightly buckled structure as compared to graphene's planar geometry. Similarly, silicon germanide (Si–Ge), an alloy of Si and Ge, also shows a slightly buckled (puckered) geometry with the angle between neighbouring bonds $\theta$ being 114.5° and the buckling parameter $\Delta$ being 0.55 Å.[5] The high temperature thermoelectric materials, silicon–germanium alloys,[6] have played a significant role in thermoelectricity which is defined as the direct conversion of heat into electricity or *vice versa* and depends on two famous mechanisms: the Seebeck effect and the Peltier effect. The main attraction towards SiGe alloys is the abundant nature of silicon and germanium and their potential compatibility with current technology of integrated circuits.[7] Furthermore, due to their non-toxicity, low-cost as compared to commercially available bulks and relatively high thermoelectric efficiency, they have long been used in radioisotope thermoelectric generators (RTGs) in NASA flights like Voyager 1, Voyager 2 and New Horizons.[8] The thermoelectric figure of merit (*ZT*) of p-type and n-type bulk SiGe alloys is 0.5 at 1073 K and 0.95 at 1173 K, respectively.[9]

SiGe has been explored in different forms like thin films,[10] amorphous structures,[11] nanotubes, nanomeshes *etc.*[12] The improvement in thermoelectric efficiency can be achieved by lowering the dimension of materials to the nanoscale, which will be responsible for increased phonon boundary scattering and decreased thermal conductivity.[13] The power factor (PF) improvement through degenerate states near the Fermi level can be attained through quantum confinement and energy filtering effects.[14] Through the nanostructuring of SiGe, an improved n-type *ZT* of ~1.3 at 1173 K and p-type *ZT* of 0.95 at 1073 K have been reported.[15,16] Recently, Fan *et al.*[17] studied the effect of electron–phonon coupling on thermoelectric properties using first principle calculations and found a reduction in lattice thermal conductivity for the SiGe bulk phase. However, this decrement in lattice thermal conductivity and inclusion of

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# Thermal transport properties of boron nitride based materials: A review

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ABSTRACT

The era of thermoelectric materials has begun in the search of clean, green and renewable anticipated energy resources. Thermoelectric materials are attracting a lot of spotlights by directly converting waste heat in electricity and could be a valuable part in world's energy emergence. Present review provides an insight into the emerging boron nitride (BN) structures on the basis of their thermoelectric properties. In the recent years, advances in the synthesis of boron nitride based structures which are analogous to carbon, have attracted significant interest by the researchers. The electronic, optical and vibrational properties of boron nitride structures are widely studied, while the thermoelectric properties have not been thoroughly investigated. However, over the past years, a significant effort has been directed towards the enhancement of their thermoelectric properties. The higher the value of figure of merit (ZT), the greater is the production of electricity. Different technologies were adopted by researchers in developing the thermoelectric efficiency. Due to the interconnection between thermoelectric parameters it is difficult to achieve ZT up to 2 or 3. Commercially existing Pb–Te and Bi–Te based thermoelectric materials provide good thermoelectric efficiency but are toxic, denser and of high cost. Therefore, there is a need of environment friendly, reusable and low cost thermoelectric materials. An extensive review of the thermoelectric characteristics of bulk phases of BN (like a-BN, c-BN, and w-BN), hexagonal-BN (h-BN), boron nitride nanotube (BNNT), boron nitride nanoribbon (ABNNR and ZBNNR), boron nitride quantum dots and boron nitride composites is presented. This evolution in boron nitride based materials will elucidate their potential for developing high-performance next-generation thermoelectric devices.

## 1. Introduction

In the recent years, owing to the world's need for managing energy crisis, thermoelectric materials play an important role in converting waste heat to the valuable electricity. Several methods are appropriate to recover waste heat including steam and organic Rankine cycle which are indirect power generation methods, absorption cooling, plant/district water heating, direct power generation like piezoelectric and thermoelectric, biomass co-location, water desalination etc. [1]. Among all these technologies, thermoelectric begun a new realm in research field to recover waste heat as this technology directly converts the thermal energy to electrical energy, unlike others. Fig. 1(a–b) presents the arising need of energy demand, while ~90% of the total power supply still relies upon fossil fuels. Moreover, 70% of energy of these fuels is unused and wasted in heat form in factories which needs giant cooling systems. Therefore, an urgency in the sustainable alternative is needed thinking the total energy consumption up to 13 billion tonnes of oil in 2015 [2]. Thermoelectricity and pyroelectricity are two main approaches to accumulate concerned heat energy. Temperature difference in materials generate an electric potential in two different semiconductors which accomplishes Seebeck effect for conversion in thermoelectricity, whereas in pyroelectricity the structure of a specific material changes when heat is enforced on them resulting in alteration of polarization developing electric potential [3]. The Seebeck effect like the Peltier effect is a predominant thermoelectric effect.

The Seebeck effect is a phenomena that shows voltage difference (ΔV) is induced in proportion to applied temperature gradient (ΔT), expressed as:

$$\Delta V = S\Delta T \quad (1)$$

where S is called the Seebeck coefficient and also known as thermoelectric power or thermopower. The Seebeck effect can be used to

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LETTER TO THE EDITOR

# The Reynolds number modulated low frequency dynamical modes of aqueous medium embedded spherical virus and implications to detecting and killing viruses

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## Introduction

The low frequency dynamical modes of nanometric viruses have been the subject of great concern in last few years (Dubrovskiy & Morochnik, 1981; Felderhof, 2014; Galstyan, Pak, & Stone, 2015; Kheisin, 1967; Pelton, Chakraborty, Malachosky, Guyot-Sionnest, & Sader, 2013; Saviot, Netting, & Murray, 2007). Viruses being one of the smallest organisms are the miniscule pockets of proteins containing RNA or DNA surrounded by capsid and have found potential applications in diverse areas of rapidly developing nanotechnologies such as nanotemplates for nanofabrication (Knez et al., 2003; Knez et al., 2004; Mao et al., 2004; Pankhurst, Connolly, Jones, & Dobson, 2003) and in diagnosing and treating the viral diseases (Duval, Saviot, David, Etienne, & Jal, 2003; Ford, 2003; Talati & Jha, 2006). Besides, nanometric viruses present in aqueous medium can be treated as microstructures which have undoubtly the great fundamental and practical interests driven by potential applications in targeted drug delivery (Ahmad & Edirisinghe, 2017). Nanometric size and approximately spherical shape of many viruses make an analogy with nanocrystals or quantum dots. The analogy between nanometric size and approximately spherical shape of many viruses has been successfully applied to use the highly celebrated Lamb's classical model of confined elastic vibrations in viruses of nanoscale size (Dubrovskiy & Morochnik, 1981; Felderhof, 2014; Galstyan et al., 2015; Kheisin, 1967; Pelton et al., 2013; Saviot et al., 2007; Talati & Jha, 2006). The confined elastic vibrations or quantized low frequency dynamical modes in nanostructures are mechanical vibrations with frequency of orders of sound divided by a typical length of the nanostructure (Saviot et al., 2007). Furthermore, these dynamical modes of nanoparticles (spherical viruses) manifest themselves in the low frequency Raman Spectra which make determination and understanding of their low frequency vibrational modes possible (Talati & Jha, 2006; Tiwari, Sharma, Jha, & Pratap, 2019). The first attempt to find frequency of these low frequency vibrational modes of a free, isotropic, homogeneous, continuous sphere using only size, density and speeds of sound in bulk material was made by Lamb (1882). However, there exist many modifications to this with the inclusion of the effect of surrounding medium (Chakraborty et al. 2013; Dubrovskiy & Morochnik, 1981; Galstyan et al. 2015; Kheisin, 1967; Pelton et al., 2013; Saviot et al., 2007). A growing interest towards the study of vibrational mode quantization of viruses is manifested to its suitability in less expensive medical applications (Ahmed et al., 2016; Bertin et al., 2015).

The estimation of vibrational frequencies in spherical virus particles or other similar organic nanostructures has been attempted previously by several workers (Dubrovskiy & Morochnik, 1981; Felderhof, 2014; Galstyan et al. 2015; Kheisin, 1967; Lamb, 1882; Pelton et al., 2013; Saviot et al., 2007). Most of these studies however have been performed by considering the spherical viruses as bare spherical nanoparticles ignoring the effect of liquid solvent. The effect of surrounding medium on the vibrational modes for any system was first presented by Dubrovskiy and Morochnik (1981). The frequency of the modes turns imaginary in the presence of surrounding medium while, the real part represents the vibration of free particle and the decay of modes due to loss of energy of vibrating particle. With the basic idea of Dubrovskiy, many investigations on the spheres present in the surrounding medium mainly the water or glycerol have been performed (Chakraborty et al. 2013; Dubrovskiy & Morochnik, 1981; Galstyan et al. 2015; Kheisin, 1967; Pelton et al., 2013; Saviot et al., 2007). These works have treated medium as an elastic medium with zero transverse speed of sound. The viscosity effect was considered for the torsional modes of vibrations for biological objects (Gennes & Papoular, 1969; Kaynak et al., 2017). This was followed by another study on TMV virus by considering the effect of viscosity on the frequency of vibrational modes (Saviot et al., 2007). The viscosity of water significantly dampens the free vibrational modes of TMV virus. Though the effect of viscosity is considered successfully, there is no consideration of effects of mutual interaction of inertial and viscous forces on vibrational modes. However, the previous studies in spite of propounding

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# Effect of aqueous medium on low-frequency dynamics, chemical activity and physical properties of a spherical virus

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**ABSTRACT**

In this work, we have studied the effect of size and aqueous medium on the low-frequency dynamics, physical properties like melting temperature and glass transition temperature and chemical properties like catalytic activation energy of spherical virus using Lindemann's criteria and Arrhenius relation under their dynamic limit. The melting temperature and catalytic activation energy decrease with decreasing size of spherical virus. The glass transition temperature which increases with decreasing size of the virus is analyzed through the size dependent melting temperature. The melting temperature and catalytic activation energy of spherical virus of particular size increases when it is embedded in glycerol or water due to mismatch of the physical properties at the interface of virus and surrounding medium. In addition, the glass transition temperature of free and glycerol/water embedded virus using low-frequency vibrational modes has been calculated under the framework of elastic continuum approximation model. The glass transition temperature of spherical virus decreases with size when embedded in glycerol or water. A correlation between $T_g$ and $T_m$ is also drawn for spherical viruses. The study can be useful for spherical virus borne therapy i.e. in detecting and killing of the spherical viruses using a principle based on acoustic phonons (sound waves) resonance.

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**KEYWORDS**
Virus; lysozyme; catalytic activity; glass transition; low-frequency phonon mode

## 1. Introduction

The minuscule living organisms viruses and bacteria occur with different shapes and sizes in nature. Nonetheless, most of the viruses tend to be in spherical shapes with diameter ranging amidst 20–100 nm. All viruses are infinitesimal pockets of protein coat (capsid) which encloses nucleic acid core composed of either DNA or RNA. These tiny viruses have found promising applications in several fields of rapidly growing nanotechnologies (Pankhurst, Connolly, Jones, & Dobson, 2003). In past years, the application of biological objects including viruses and bacteria as nanotemplates in nanofabrication was acquired (Alonso, Górzny, & Bittner, 2013; Flynn, Lee, Peelle, & Belcher, 2003; Górzny, Walton, & Evans, 2010; Park et al., 2016; Shenton, Douglas, Young, Stubbs, & Mann, 1999). For instance, tobacco mosaic virus (TMV) and M13 bacteriophage were successfully used in the synthesis of metallic and semiconductor nanowires (Shenton et al., 1999). For nanomaterial's self-assembly, inherently mutated TMV and M13 were well used (Flynn et al., 2003). Furthermore, the physical properties of TMV make it an attractive molecule for engineering hybrid materials (Alonso et al., 2013). Metal-coated TMVs have been used as a structural component in nickel-zinc and lithium ion batteries while TMV coated with fine platinum is a promising anode material for direct methanol fuel cells (Gorzny, Walton, & Evans, 2010). The utilization of viruses commonly occurs in two categories (i) major fabrication for bulk devices such as energy generation/storage, or ferrofluids; (ii) manufacturing of fine layers or wires for biosensors in the form of small quantity (Alonso et al., 2013). The researchers have successfully used genetically engineered viruses in contrast to the usual high-tech materials or microchips to harvest solar energy (Park et al., 2016). In addition, the common viruses have been found useful in producing materials that resemble skin and bone (Chung et al., 2011). The evaluation of physical and chemical properties of viruses has been extensively explored (Ghavanloo & Fazelzadeh, 2014; May, 2014; Talati & Jha, 2006) and topic of interest due to their budding use in nanotechnology and therapeutics. An insight in their mechanism is gaining many attentions in order to utilize them in nanotechnology (Aggarwal, May, Brooks & Klug, 2016; Lošdorfer Božič & Šiber, 2018; Zhang & Zhang, 2018). Our study will help in making predictions about biological phenomena and determining their properties relevant to nanotechnology design efforts and new therapeutic targets. Through low-frequency vibration analysis one can find its application in diagnosis/treatment of various viral diseases. The concept of killing and destroying viruses can be supported by the Rife therapy performed by a Rife frequency instrument, which destroys the microbe when there is a resonance between the mechanical oscillation frequency. The existence of well-defined resonance has also been emphasized by Ford (2003) for which the knowledge of damping

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# Role of $CuAlO_2$ as an absorber layer for solar energy converter

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ABSTRACT

A delafossite semiconductor, namely $CuAlO_2$, with a lower band gap is a potential candidate for the absorption of solar radiation due to its excellent electronic and optical properties. In this paper, structural, electronic, vibrational and optical properties of delafossite $CuAlO_2$ have been calculated using state-of-the-art first principles calculations based on density functional theory (DFT). The optimized structural parameters, electronic properties and Raman active vibrational modes namely the $E_g$ and $A_{1g}$ are in good agreement with experimental and other theoretical data. The full phonon dispersion curves (PDC) together with the phonon density of states (PHDOS) of $CuAlO_2$ depict its dynamical stability due to non-existence of any imaginary phonon mode in the entire Brillouin zone (BZ). To understand the mechanism of optical transition properties, we have further calculated the dielectric functions, absorption coefficient and joint density of states (JDOS) for delafossite, $CuAlO_2$. The dielectric constant and absorption coefficient show a significant anisotropic nature in the components of polarization directions. Solar cell parameters of $CuAlO_2$ are also calculated and the highest theoretical efficiencies of 14.8% and 12.5% have been observed with Shockley-Queisser (SQ) limit and spectroscopic limited maximum efficiency (SLME) respectively. The SLME predicted efficiency agrees better to the experimental value as it includes the thickness dependent absorbance coefficient in account of non-radiative recombination and carrier loss mechanism.

## 1. Introduction

The past few decades were dedicated to the study of transition metal oxides for solar cell applications (Gao et al., 2018). Most of the solar cells and optical devices are based on the n-type materials (Nomura et al., 2002; Park et al., 2006; Popovich et al., 2003). However, applications such as light emitting diode (LED) and functional windows require both n and p-type materials. Recently, the p-type semiconductors are widely studied because they can combine with n-type to form a p-n junction diode useful in many applications including dye sensitized solar cells (DSSCs) (Zhang et al., 2017). The NiO based p-type semiconductor was studied which gives excellent results when combined with n-type materials such as $TiO_2$ (He et al., 2000; Odobel et al., 2010). However, NiO has some limitations due to its narrow band gap, significant absorption of sun light, and low hole mobility (Nattestad et al., 2010). The p-type semiconductors such as CuO (Sumikura et al., 2008), CuScN (Fernando et al., 1994), have been studied but they hardly show the solar cell power conversion efficiency (PEC). Therefore, the study of new p-type semiconductor materials in the form of complex oxides arises for DSSCs due to its tunable properties (Tan et al., 2007). In this context, copper (Cu) based delafossite type oxides having p-type conductivity are used for DSSCs applications (Ahmed et al., 2014). The Cu based delafossites are expected to have a small band gap due to higher energy valence band (VB) edge arising from $d^{10}$ configuration of $Cu^{2+}$ ions (Tablero Crespo, 2018). Amongst them $CuAlO_2$ with a delafossite structure is a first p-type semiconducting material which is useful in transparent conducting oxides (TCOs) (Kawazoe et al., 1997). Further, many delafossite type structure-based p-type materials such as $CuGaO_2$, $CuFeO_2$, $CuScO_2$, and $CuInO_2$ etc. were developed and their technological importance was highlighted. Among the different materials developed so far, $CuAlO_2$ is most fascinating and attractive delafossite due to the coexistence of p-type conductivity and transparency in visible light. Its different properties and related technological aspects have been investigated by many researchers, (Banerjee and Chattopadhyay, 2005). The lower band gap in $CuAlO_2$ makes it interesting for absorbing the solar radiation in solar conversion, photovoltaics or photoelectrochemical. Further, the delafossite type compounds are useful candidate for DSSCs. Recently, Tablero Crespo (2018) studied the possibilities of $CuFeO_2$ and $CuRhO_2$ as solar cell convertors, by calculating the absorption coefficient. The

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FULL PAPER

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# Graphene Oxide Supported Oxovanadium (IV) Complex for Catalytic Peroxidative Epoxidation of Styrene: An Eye-Catching Impact of Solvent

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Graphene oxide (GO) supported transition metal complexes are apprised as sturdy and everlasting heterogeneous catalysts. GO surface was functionalized with 3-triethoxysilylpropylamine (TSPA) and this amino functionalized GO (A-*f*-GO) nanocomposite with vanadyl Schiff base complex (VO-*f*-GO) was prepared and to give credence of its potentiality, it was chosen for the selective epoxidation of styrene using environmentally benign 30% $H_2O_2$ to styrene oxide (SO). To evade the detrimental exposure of "*inborn*" water, a selective high boiling and potent hygroscopic solvent, ethylene glycol was chosen to make this transformation productively successful. With the assistance of theoretical studies, we have probed the effect of $H_2O_2$ on to structural properties, binding mechanism and electronic properties of the catalyst and substrate. Adsorption energy ($E_{ad}$), energy band gap ($E_g$) and HOMO-LUMO were also calculated. Based on DFT calculations, resonance Raman and UV/Vis studies, we confirmed the formation of metal-peroxo species and propose the plausible catalytic pathway. The influence of the diverse experimental parameters, like substrate to oxidant mole ratio, catalyst concentration, type of solvents, solvent amount, time, temperature and oxidant were tested. A clear relationship was found between different reaction parameters like solvent amount, oxidant, catalyst concentration and temperature etc. and product distribution. This heterogeneous catalyst yielded styrene oxide as nearly the sole product (selectivity = 98.7%) with a conversion value of 99.2% in the oxidation of styrene with hydrogen peroxide in ethylene glycol.

KEYWORDS

density functional theory, GO supported heterogeneous catalyst, peroxidative epoxidation of styrene, solvent effect

## 1 | INTRODUCTION

Catalytic oxidation of hydrocarbons is "nitty-gritty" for the industrial production of chemicals. Amongst them, catalytic epoxidation of olefins is even of the utmost prominence, particularly in the pharmaceuticals and fine chemical industries. Epoxides, the oxidized product of olefins are considered to be the most adaptable raw material in scores of organic synthesis[1] due to partly positive carbon and a Lewis-basic oxygen atom in a three-