Computational study of dielectric function and optical properties of a graphane nano structure containing graphene quantum dot

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Abstract: Ab-Initio computational study of dielectric function and optical properties of a graphane nano structure containing graphene quantum dot has been undertaken within Density Functional Theory using SIESTA code. Band structure, PDOS, real and imaginary parts of dielectric function, reflectance and energy loss have been calculated and frequencies corresponding to peak positions have been tabulated for each case. A comparison has been made with the corresponding properties of pristine graphene.

Keywords: Quantum Dots, Density Functional Theory, SIESTA, Electronic Density of States, Optical Properties, Dielectric Function.

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1. Introduction

Graphene [1-6], a 2D crystal, is an allotrope of carbon with atoms arranged in a regular hexagonal pattern similar to graphite but in a one-atom thick planar sheet of sp²-bonded carbon atoms that are densely packed in a honeycomb crystal lattice. It has gained attention due to unique electronic and optical properties [6-9]. Graphene exhibits fascinating properties such as a relativistic massless-dispersion for its charge carriers and ballistic transport on large distances. In addition to numerous experimental and theoretical studies on the physical properties of graphene, efforts have been to synthesize various types of derivatives of graphene such as graphane [6, 10-17]. The first theoretical description of graphane was reported in 2007 [10] and its preparation was reported in 2009 [11].

Graphane is a 2-dimensional polymer of hydrogenated graphene with the formula unit (CH) repeated periodically. Full hydrogenation from both sides of a graphene sheet results in graphane but partial hydrogenation leads to hydrogenated graphene.

The introduction of a cluster of vacancies in hydrogen sub lattice of graphene leads to formation of graphene quantum dots (QD’s) [18]. QD’s or artificial atoms are one of the most intensely studied systems [19]. QD’s have enormous potentials for applications ranging from novel lasers to quantum information processing. Here we explore the electronic and optical response of QD’s as vacancies in hydrogen sub lattice of graphene.

In the present work ab initio computational study of nano structures of graphene (50C atoms, 5x5x1 super cell) and graphene containing graphene QD (50C+38H atoms in chair conformation) [figure 1(a-c)] has been undertaken within Density Functional Theory using SIESTA code. QD, a cluster of vacancies in hydrogen sub lattice, was modelled by pulling out hydrogen atoms from graphene. Band structure, PDOS, real and imaginary parts of dielectric function, reflectance and energy loss have been calculated and frequencies corresponding to peak positions have been tabulated for each case. A comparison has been made with the corresponding properties of pristine graphene.
2. Computational Details

In this work, we have used Troullier Martin, norm conserving, relativistic pseudopotentials in fully separable Kleinman and Bylander form for Carbon and Hydrogen. Our calculations have been performed in the framework of Density Functional Theory within the generalized gradient approximation (GGA) according to the Perdew, Burke, Ernzerhof (PBE) parameterization using SIESTA code and methods [20, 21]. The graphene sheet is described within the supercell (5x5x1) approach, by a single layer of graphene with 50C atoms. Interaction between adjacent layers is hindered by a large spacing of ~20 Å. A 250 Ry mesh cutoff has been used for the reciprocal space expansion of the total charge density. Brillouin zone has been sampled by using 11×11×1 Monkhorst-Pack of k points. Localized atomic orbitals basis set has been used with confinement energy of 0.02 Ry. Minimization of energy is carried out by giving sufficient number of SCF iterations using standard conjugate-gradients technique [20, 21]. Optical calculations have been carried out using 33x33x3 optical mesh and 0.2 eV optical broadening.

3. Results and discussion

3.1 Electronic Band Structure and Interband Transitions

The figure 2 (a & b) shows the plots of band structure and partial electron density of states (PDOS) for pristine graphene [figure 2(a)] and graphene having graphene QD [figure 2(b)]. The band gap decreases with the introduction of a cluster of vacancies in hydrogen sub lattice of graphene.

![Figure 1](image1.png)

**Figure 1** Optimized structures of (a) Pristine Graphene (b) Pristine Graphane, 50C+50H atoms (c) Graphane containing Quantum Dot, 50C+38H atoms.

![Figure 2](image2.png)

**Figure 2** Band Structure and Electron Density of States for (a) Pristine Graphene (b) Graphane having QD [Here A, B, C….. : show electronic transitions which correspond to peak positions in the spectrum of optical parameters.]
Calculated multiple sharp peaks near the Fermi energy show the characteristic of quantum dot as an artificial atom. It is clear from the plots of PDOS that the multiple peaks near Fermi energy are due to C\textsubscript{2p}\textsubscript{z} electrons [figure 2(b)]. The lines A, B & C in figure 2(a) show the electronic transitions which correspond to peak positions in the spectrum of optical parameters at frequencies 4.0 eV, 13.63 eV and 14.49 eV respectively (table 1) for pristine graphene. The peak near 4.0 eV is approximately associated with the transition from valance band near -2.50 eV to conduction band near 1.50 eV while peak at 13.63 eV is associated with the transition from valance band near -6.4 eV to conduction band near 7.23 eV. The peak near 14.49 eV is approximately associated with the transition from valance band near -6.40 eV to conduction band near 8.10 eV.

The figure 2(b) shows the band structure and partial electron density of states (PDOS) for graphane containing graphene QD. The lines A, B, C, D, E & F in figure 2(b) show the electronic transitions corresponding to peak positions in the spectrum of optical parameters at frequencies 1.43 eV, 3.54 eV, 8.10 eV, 4.97 eV, 6.27 eV and 10.09 eV respectively (table 1). The peak near 1.43 eV is approximately associated with the transition from valance band near -0.68 eV to conduction band near 0.63 eV while peak at 3.54 eV is associated with the transition from valance band near -1.59 eV to conduction band near 1.86 eV. The peak near 8.10 eV is approximately associated with the transition from valance band near -3.58 eV to conduction band near 4.62 eV while the peak near 4.97 eV is approximately associated with the transition from valance band near -1.85 eV to conduction band near 3.12 eV. The peak near 6.27 eV is approximately associated with the transition from valance band near -2.81 eV to conduction band near 3.02 eV while the peak near 10.09 eV is approximately associated with the transition from valance band near -4.85 eV to conduction band near 5.20 eV.

3.2 Optical Properties
3.2.1 Real & Imaginary parts of dielectric function
The figure 3(a) shows the plot of real part of dielectric function spectrum for in-plane polarization (E\textsubscript{\perp}c) and out-of-plane polarization (E\textsubscript{||}c) for pristine graphene (red curve) and graphane containing graphene QD.

![Figure 3](image)

**Figure 3** Plot of (a) Real part of dielectric function (\(\varepsilon_1\)), (b) Imaginary part of dielectric function for in-plane polarization (E\textsubscript{\perp}c) and out-of-plane polarization (E\textsubscript{||}c) for pristine graphene (red curve) and graphane containing graphene QD (black curve).

In the case of pristine graphene, for in-plane polarization (E\textsubscript{\perp}c), there is a dip in the amplitude of the real part of dielectric function and it attains a small negative value at 4.8 eV indicating that there is
plasmonic excitation near 4.8 eV. Also dip in $\varepsilon_1$ at 14.49 eV and 17.01 eV for $E \parallel c$ and 13.63 eV for $E \perp c$ indicate plasmons excitations at these energies.

Corresponding to graphene having graphene QD, the dip in $\varepsilon_1$ at 10.54 eV and 14.04 eV for out-of-plane polarization ($E \parallel c$) while at 1.47 eV, 4.97 eV and 10.09 eV for in-plane polarization indicate plasmons excitations at these energies.

The figure 3(b) shows the plot of imaginary part of dielectric function ($\varepsilon_2$) for in-plane polarization ($E \parallel c$) and out-of-plane polarization ($E \perp c$) for pristine graphene (red curve) and graphane containing graphene QD. Corresponding peak positions are given in table 1. For in-plane polarization, in pristine graphene, peaks appear at 4.0 eV and 13.63 eV, which are in good agreement with recent plane wave calculated results (4.0 eV and 13.8 eV) [7] and experimentally observed values 4.6 eV and 14.6 eV [8]. For ($E \parallel c$), the spectrum of imaginary part of dielectric function shows peaks at 14.49 eV and 17.01 eV [figure 3(a)] for pristine graphene.

For graphane containing graphene QD, the peaks are observed at frequencies 1.43 eV, 3.54 eV, 8.34 eV & 13.79 eV for out-of-plane polarization while at frequencies 1.39 eV & 4.81 eV for in-plane polarization.

3.2.2 Reflectance spectrum & Electron Energy Loss (EEL)

The figure 4(a) shows the plot of reflectance spectrum for in-plane polarization ($E \perp c$) and out-of-plane polarization ($E \parallel c$) for pristine graphene (red curve) and graphane containing graphene QD. For out-of-plane polarization in pristine graphene peaks appear at 14.58 eV and 17.29 eV, while for graphane containing graphene QD peaks appear at frequencies 8.1 eV and 13.96 eV. For in-plane polarization in pristine graphene peaks appear at 4.31 eV and 13.80 eV, while for graphane containing graphene QD peaks appear at frequencies 1.39 eV and 4.81 eV.

The figure 4(a) shows the plot of electron energy loss (EEL) spectrum for in-plane polarization ($E \perp c$) and out-of-plane polarization ($E \parallel c$) for pristine graphene (red curve) and graphane containing graphene QD.

Electron energy loss (EEL) function is proportional to the inverse of dielectric function and corresponds to the collective excitations of electrons of system. In the case of pristine graphene a sharp resonance peak at 5.12 eV and relatively broad peak around 15.16 eV have been found for in-
plane polarization (E⊥c) (see figure 4(b)), which are in very good agreement with recently calculated plane wave results 4.8 eV and 15.0 eV [7] and also with experimentally measured values of 4.7 eV and 14.5 eV respectively [8]. For out-of-plane polarization (E∥c) resonance peaks have been found at 14.72 eV and 17.29 eV, while a plane wave calculation reveals resonance at 11.7 eV and 14.7 eV [7]. For graphene containing graphene QD, the sharp peaks are observed at frequencies 1.43 eV, 8.83 eV & 14.12 eV and a broad peak is observed around 10 eV for out-of-plane polarization. For in-plane polarization sharp peaks are observed at frequencies 1.47 eV, 3.50 eV, 4.97 eV, 6.27 eV & 10.09 eV. Thus new sharp peaks appear in the frequency region of 0 eV to 5 eV for graphene containing graphene QD for in-plane polarization.

Table 1 shows the peak positions in eV for imaginary part of dielectric function, reflectance and electron energy loss in case of out-of-plane polarization (E∥c) and in-plane polarization (E⊥c) for pristine graphene and graphene containing graphene quantum dot (GQD).

### 3.2.3 Red Shift in Peak Frequencies
It is found that there is red shift in plasmonic resonance frequencies in the case of graphene nanostructure containing graphene QD as compared to pristine graphene, although the shifts in the peaks are not uniform as can be seen in figure 4(b) and table 1. As compared to pristine graphene, the spectra of dielectric function show red shift of 0.56 eV for out-of-plane polarization (E∥c) and 3.74 eV for in-plane polarization (E⊥c). In EEL spectrum the red shift of 0.60 eV has been found for E∥c while red shift of 0.15 eV for E⊥c.

Table 1: Peak positions in eV for imaginary part of dielectric function, reflectance and electron energy loss in case of polarization parallel to c and perpendicular to c for pristine graphene and graphene containing graphene quantum dot. (GQD: Graphane containing graphene quantum dot)

| Optical Properties | System       | Peak Positions when E∥c (in eV) | Peak Positions when E⊥c (in eV) |
|-------------------|--------------|---------------------------------|---------------------------------|
|                   |              | Our simulation                  | Others                          |
| Imaginary part of dielectric function | Pristine Graphene | 14.49, 17.01                   | 4.0, 13.63                      |
|                   | GQD          | 1.43, 3.54, 8.34, 13.79         | 4.0, 13.63, 4.6, 14.6 [8]       |
| Reflectance Spectrum | Pristine Graphene | 14.58, 17.29                   | 4.31, 13.80                     |
|                   | GQD          | 8.10, 13.96                     | 1.39, 4.81                      |
| Electron Energy Loss Spectrum | Pristine Graphene | 14.72, 17.29                   | 5.12, 15.16                     |
|                   | GQD          | 1.43, 8.83, 14.04               | 1.47, 3.50, 4.97, 6.27, 10.09   |

4. Conclusions
In conclusion, we have performed first principle calculations to study the dielectric function and change in optical response of graphene nanostructure containing graphene QD as compared to pristine graphene.
In the band structure band gap appears near the Fermi energy which is found to be 5.23039 eV in pristine graphane (50C+50H) and 1.36846 eV in graphane containing graphene QD. In the plot of PDOS multiple peaks are observed near the Fermi energy which are due to C\_2p\_z electrons. As compared to pristine graphene, the peak position in the spectra of dielectric function shows red shift of 0.56 eV for out-of-plane polarization (E || c) and 3.74 eV for in-plane polarization (E \perp c). The peak intensities are reduced as compared to pristine graphene. The graphane nano structure having graphene QD is optically more active in the visible region showing additional peaks between 0 eV to 5 eV as compared to pristine graphene.

These electronic and dielectric properties of graphane nanostructure containing graphene QD can be useful for the applications in microelectronics and optoelectronic devices.

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