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A DFT study of structural, electronic and optical properties of heteroatom doped monolayer graphene

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ABSTRACT

In this paper we present a theoretical work on the influence of doped and co-doped *Al, Al-S, Al-N* and *Al-P* heteroatoms in the mono layer graphene surface. The Density functional study reveals that, *Al*, *P* and *S* co-doping significantly modifies the neighborhood bonding arrangement of the graphene sheet. The Natural population analysis revels that *Al*, *P* and *S* co-doping makes the graphene surface as electron rich system. From the molecular orbital analysis it is found that HOMO-LUMO energy gap decreases by starting from the pristine graphene in following manner *Al* doping > *Al-S* co-doping> *Al-N* co-doping >*Al-P* co-doping. On the other hand, the time dependent density functional theory (TD-DFT) calculation shows that the maximum absorbing wavelength of *Al-P* and *Al-N* co-doped graphene systems shifted towards the lower wavelength range with respect to *Al* doped graphene.

1. Introduction

The modern age has been significantly influenced by nanoscience and nanotechnology. Due to having amazing and fascinating properties, nanostructured materials are being widely used in various field of applications [1–3]. Carbon-based nanostructured materials got much attention from material researchers from the last thirty years. Among all the structures Graphene is one of the promising materials which is broadly utilized today. From the historical perspective, single layer of graphite was observed and termed as graphene by the International Union of Pure and Applied Chemistry in 1995 [4]. But, it was mechanically exfoliated by Novoselov in 2004 [5]. The excellent electronic, optical, thermal and mechanical properties [6–8] made graphene a unique structure compare to other nanostructure materials. Apart from this, Graphene also shows many fantastic properties such as high specific surface area, high carrier mobility at room temperature and high Young's modulus etc. However, sometimes the fundamental properties of the graphene need to be tuned, so as to get the application in the desired field. Therefore, combination of graphene with other materials like metals, semiconductors, polymers, ceramics, biomaterials and even liquids, changes the properties of graphene [9–11]. Doping is yet another pioneer effective process through which these properties can be altered.

In the recent years, photovoltaic and optoelectronic devices are being extensively used in many applications. But, the conversion efficiency is one of the major problem, because that affects the overall performance of the devices. Therefore, to enhance the efficiency of such devices, different methods have been introduced like surface passivation, antireflective coatings, etc. [12,13]. In addition to that, to enhance the photocurrent, hybrid photodiodes made by graphene semiconductor hetero junctions are being used [14]. Moreover, Review of literature shows that graphene itself can also be used as a light

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absorbing material [15–17]. Wang et al. [18] investigated the optical properties of graphene quantum dots and found that surface functionalization with donor or acceptor groups produce a red shift in the absorption spectrum. On examining the absorption /emission properties of graphene quantum dots Kim et al. [19] found that with varying the average size of GQDs from 5 to 35 nm, the peak energy of the absorption spectra decreases. In another work Gupta et al. [20] demonstrated that combination of graphene quantum dots with polymer material provides a significant improvement in the organic photovoltaic characteristics. Till that, a very few studies have been reported about the optical characteristics of heteroatom doped graphene. In this work, we investigated how structural, electronic and optical properties of pristine graphene changes when it is doped with *Al*, *Al-N*, *Al-P* and Al-S dopant. Our calculation revels that *Al*, *Al-P* and *Al-S* doping improves the graphene surface as more electron rich system. On the other hand the absorption spectra of *Al-P* and *Al-N* co-doped graphene is shifted towards the lower wavelength range with respect to *Al* doped graphene.

2. Computational details

In this work, all computational simulations are performed using density functional theory under Gaussian 09 package [21]. Here, Becke, 3-parameter, Lee-Yang-Parr [B3LYP] exchange correlation functional [22] and 6–31 G (d) basis set is used. The same computational scheme has also been used by many researchers [23–25]. Here, the graphene sheet is designed, using 7 hexagonal rings and total 36 number of atoms out of which 24 atoms are Carbon and 12 atoms are hydrogen. Hydrogen atoms are added so as to avoid the dangling bonds in the boundary of graphene sheet and hence, no edge effect is considered. Geometry optimization along with the frequency calculation of undoped graphene is carried out with no symmetry constraint and no imaginary frequencies have been found, which confirm the presence of minimum energy in the system. The optimized graphene is then individually doped with *Al, Al-N, Al-P* and *Al-S.* The principle objective of this work is to see how *Al, N, P* and *S* co-doping affects the structural, electronic and optical properties of graphene.

3. Results and discussions

3.1. Optimized structures

At first here we have designed a model of pristine single layer graphene using 7 hexagonal rings and total 36 numbers of atoms, out of those 24 atoms are Carbon and 12 atoms are hydrogen. This model is geometrically optimized and obtained final structures are shown in Fig. 1(a). Now, to obtain the energetically most favorable doped graphene structures on the carbon surface we consider two different doping sites C0 and X, surrounded by C1, C2, C3 and C4, C5 and C6 respectively [Fig. 1(a)]. After that *Al* is doped by replacing the carbon atom as denoted by C0 in Fig. 1(b) and then the structure is optimized. In this case we have chosen *Al* doped graphene as the basic model. Further, this model is co-doped with *N, P* and *S* atom individually by replacing the 'X' position of the graphene sheet and then we have again optimized the structures as shown in Fig. 1(c)–(e). Structural distortions are occurred on the C surface when *Al, N, P* and *S* atoms are used as a dopant. For that the Al-C bond ($\sim$ 1.87 Å) is found longer than compare to the C—C bond in pristine graphene ($\sim$ 1.4 Å) as well as X—C bond (where X=*N, P* and *S*) which is around 1.39 Å, 1.75 Å and 1.79 Å in *N, P* and *S* respectively in the co-doped graphene. The detailed bond lengths and bond angles for all these structures are given in Tables 1 and 2 respectively. The bond angle of ∠C-Al-C, in *Al* doped graphene is found to be $\sim$106.13° and for ∠C-P-C and ∠C-S-C is found to be 109° and 103° respectively which is less than compare to the bond angle of ∠ C—C—C ($\sim$120°) in the pristine graphene. As a result the position of the *Al, P* and *S* is shifted outwards from the surface. However in the case of *Al* and *N* co-doped graphene the angle of ∠C-*N*-C is found to be $\sim$ 121° which is close to the angle of pristine graphene, hence *N* doped graphene causes less planner distortion on the graphene surface. The above results show that *Al, P* and *S* individually effects the local bonding environment of the graphene surface due to their difference in covalent radii (0.76 Å, 1.21 Å, 0.71 Å, 1.07 Å, and 1.05 Å for C, Al, N, P and S respectively) [26] and electro negativities (2.5, 1.5, 3, 2.1 and 2.5 for C, *Al, N, P* and *S* respectively) [27].

Table 1
The length of bonds in Å (Al-G and Al-X-G systems (where X=N, P and S)).

	Al-C1	Al-C2	Al-C3
Al-G	1.84	1.87	1.84
	N-C4	N-C5	N-C6
Al-N-G	1.39	1.39	1.39
	P-C4	P-C5	P-C6
Al-P-G	1.75	1.74	1.75
	S-C4	S-C5	S-C6
Al-S-G	1.78	1.79	1.78