Adsorption of Nucleobases on Different Allotropes of Phosphorene

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Abstract. There has been tremendous interest in low-dimensional quantum systems during past two decades, fueled by a constant stream of striking discoveries and also by the potential for, and realization of, new state-of-the-art electronic device architectures. In this paper, our work includes the structural, electronic and optical properties of nucleobase (Adenine(A), Cytosine(C), Guanine(G), Thymine(T)) adsorbed on different allotropes of phosphorene (α, β, γ). From the optical absorption spectra of different nucleobases when adsorbed on the surface of phosphorene, we could optically probe different Nucleobases. As phosphorene shows different spectra for different nucleobases, it behaves as a bio-sensor to detect various nucleobases.

INTRODUCTION

The interaction of DNA nucleobases with monolayer surfaces have attracted great attention because of its importance in the detection of biomolecules, specifically, nucleobases [1-3]. In particular, the development of cost-effective and efficient selective detection in future generation biosensing devices are the need of the hour. Various studies for the adsorption of four DNA nucleobases [adenine (A), cytosine (C), guanine (G) and thymine (T)] on graphene has been performed [1-2] to explore the applications of graphene-based devices for DNA biosensing. Graphene offers high flexibility and device scalability but still possess lower sensitivity to biosensing due to the lack of band gap. Phosphorene has been emerged as alternative to graphene for various nanoscale device applications due to the presence of inherent band gap [4]. Phosphorene exists in various allotropic forms in monolayer limit [5]. Note that bulk phosphorous exhibit different allotropic forms such as black phosphorous, blue phosphorous, red phosphorous etc.

In this paper, we have investigated the adsorption of four nucleobases (A, C, G, T) on three monolayer allotropes of phosphorene i.e. α- , β- and γ-phosphorene. Binding energy and charge transfer analysis has been performed. Electronic band structures and optical properties of both pristine and adsorbed monolayer have been analyzed in details.

COMPUTATIONAL DETAILS

The first principle calculation is performed using SIESTA code [6] which is based on Density Functional Theory. Numerical atomic orbital type of basis set is used with a cutoff energy equal to 250 Ry for double zeta polarized basis set. Perdew-Burke-Emzerhof (PBE) semi-local exchange-correlational functional is used to describe exchange

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and correlation effects. We use grid of 5x5x1 k-points of reciprocal space by a monkhorst pack to optimize the structure of allotropes of phosphorenes and nucleobases. The maximum force tolerance is 0.04 eV/Å. After performing the above calculations of structural optimization, we get relaxed coordinates. Using these lattice coordinates and vectors we perform the calculation for electronics and optical properties of structures. We use Gauss-view for modeling the structure of phosphorenes and Nucleobases (A, C, G, T).

RESULTS AND DISCUSSIONS

In order to model the structure for different allotropes of phosphorene, first we consider the unit cell and expand it in the x and y directions to make supercell of almost equal cross-sectional area . The α-, β- and γ-phosphorene supercell contains 64, 40, 48 phosphorus atoms, respectively. α- and γ-phosphorene possess rectangular structure whereas β- phosphorene exhibit hexagonal structure [Figure1]. In the structure of nucleobases, A nucleobase contains five carbon, five hydrogen and five nitrogen atoms; T contains five carbon, six hydrogen, two nitrogen and two oxygen atoms; G nucleobase has highest no. of atoms in which five carbon, five hydrogen, five nitrogen and one oxygen atoms; and C has lowest no. of atoms which consists of four carbon, five hydrogen, and three nitrogen and one oxygen atoms.

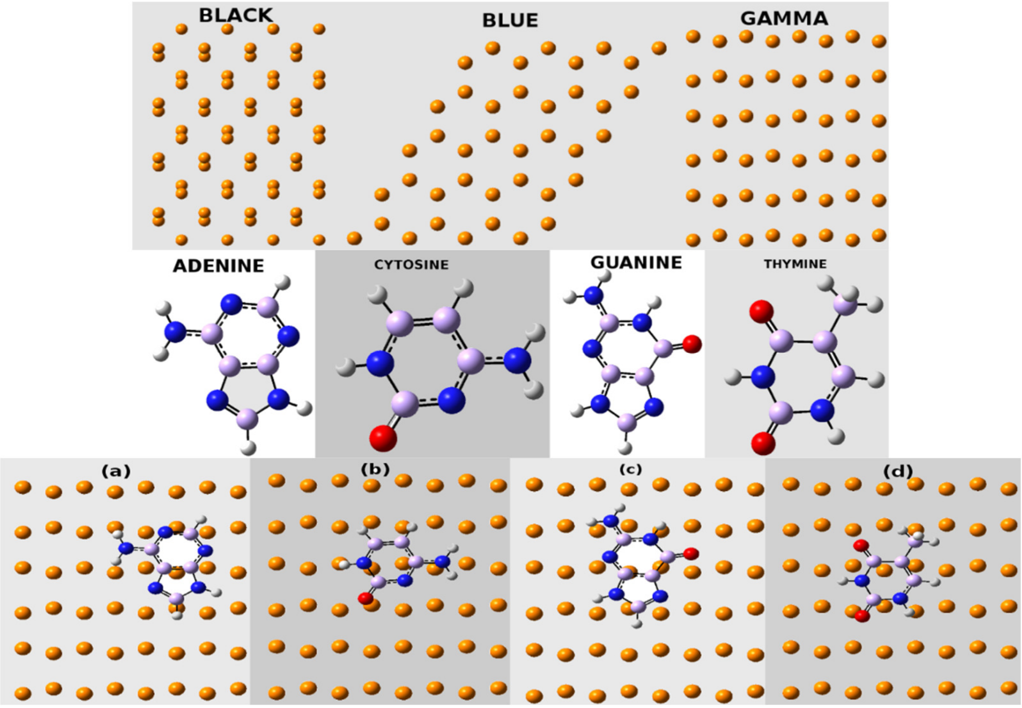

FIGURE 1. Top view of different allotropes of phosphorene (top panel). Structure of different nucleobases (middle panel). As a representative case, different nucleobase adsorption geometry (a) adenine (b) cytosine (c) guanine (d) thymine on γ-phosphorene is shown in bottom panel.

To check the stability of adsorption of different nucleobases on phosphorene, we calculate binding energy (B.E.). The binding energy of nucleobases to phosphorene is given by

$$B.E = E_{N@P} - E_N - E_P \quad \text{...(1)}$$

where, $E_{N@P}$ represents the total energy of composite structure (nucleobases @ phosphorene), E_N represents the energy of nucleobase, E_P represents the energy of phosphorene supercell. The B.E of various nucleobase absorbed on different types of phosphorene is tabulated in Table 1. The (-ve) sign indicates the stability for all the cases. Our results show that all the nucleobases bind strongly with β-phosphorene compared to α and γ phosphorene. We also did Milliken population analysis for charge transfer phenomenon. The charge transfer from A to β phosphorene is highest corresponding to its highest binding strength as shown in Table 1.

TABLE 1. Binding energy (eV) and charge transfer (in the units of electron charge) for different nucleobases adsorbed on posphorene allotropes. Values given in bracket indicate charge transfer.

Structure	Adenine	Cytosine	Guanine	Thymine
Black (α)	-1.05 (0.068)	-1.42 (0.182)	-1.37 (0.154)	-1.00 (0.083)
Blue (β)	-3.99 (0.418)	-2.66 (0.061)	-1.63 (0.174)	-2.46 (0.077)
Gamma (γ)	-1.14 (0.13)	-1.31 (0.275)	-1.32 (0.149)	-1.06 (0.074)

Electronic Properties

The electronic band structures for α-, β- and γ- phosphorene are shown in Figure 2. We find a direct band gap of 0.81 eV for pristine α phosphorene. The β phosphorene shows an indirect band gap of 2.0 eV whereas the γ phosphorene shows a direct band-gap of 0.55 eV. The band gap for A@α, C@α, G@α and T@α are 0.80 eV, 0.81 eV, 0.75 eV and 0.78 eV, respectively. It is found that for blue (or β) phosphorene, absorption of nucleobases modify the band structure in a great extent. The band gap for A@β is 0.77 eV, for C@β 1.43 eV, for G@β 1.76 eV and for T@β 1.36 eV. For nucleobases@γ-phosphorene, the band gap for A@γ is 0.60 eV, for C@γ 0.6094 eV, for G@γ 0.59 eV and for T@γ 0.59eV. Hence, the band gap gets modified when we place the nucleobases on various allotropes of phosphorene.

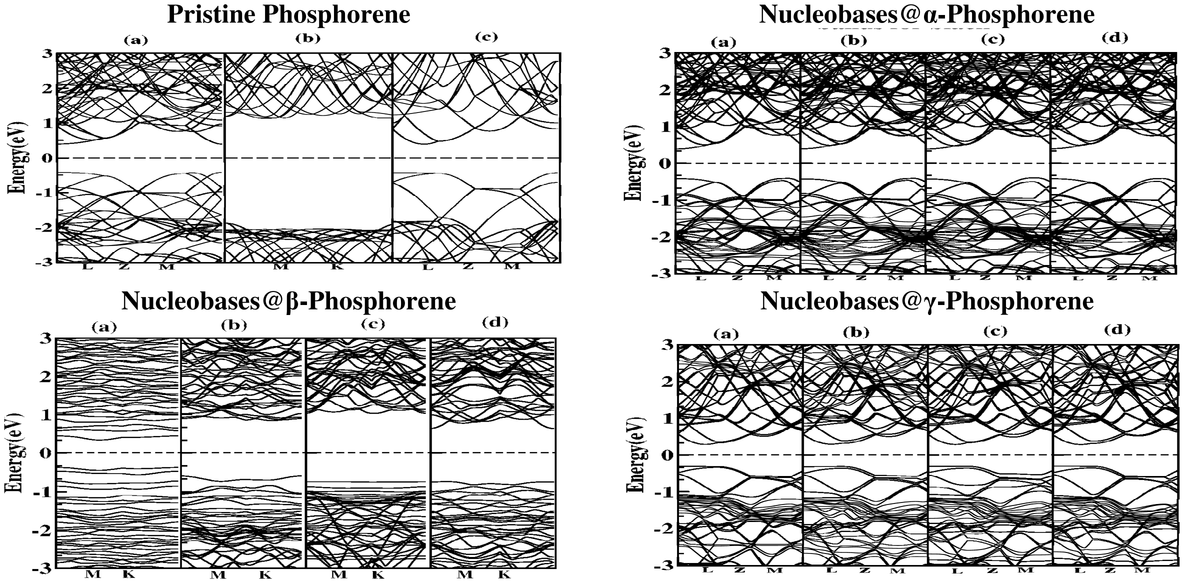

FIGURE 2. Electronic band structures of pristine phosphorene [(a) α-phosphorene (b) β-phosphorene and (c) γ-phosphorene] and different nucleobases [(a) adenine (b) cytosine (c) guanine (d) thymine] adsorbed on different allotropes of phosphorene.

Optical Properties

The imaginary part of the dielectric function is an effective parameter to measure the optical absorption of materials. We investigate the imaginary part of the dielectric function of the systems when subjected to linearly polarized light along X and X-Y direction. For pristine α-phosphorene, we get absorption band in the region of the 1.65 to ~ 10 eV, 0.75 to ~ 10 eV for linearly polarized light along X and X-Y direction, respectively. For pristine β-phosphorene, we get the wide absorption bands [Figure 3]. For pristine γ phosphorene, we get the absorption band in the region of 2.07 to ~ 9.7 eV and 2.08 to ~ 9.7 eV for linearly polarized light along X and X-Y direction respectively.It is found that the absorption edges get shifted towards lower energy (red shift) when nucleobases adsorbed on β-phosphorene. Similarly, other monolayer allotropes show modification in the dielectric spectra on the adsorption of nucleobases.

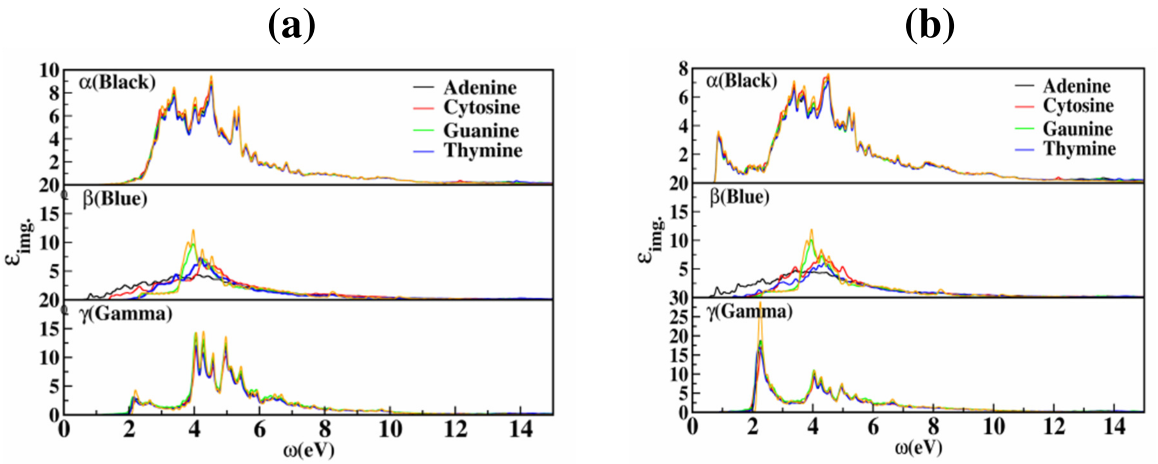

FIGURE 3. Imaginary part of dielectric function ($\varepsilon_{\text{img.}}$) for light polarized along (a) X-direction (b) X - Y direction. Orange color line represent pristine phosphorene.

SUMMARY AND CONCLUSIONS

DFT based study has been performed to obtain the results for structural, electronics and optical properties of phosphorene and nucleobase. The lowest binding energy for blue phosphorene (β) with Adenine nucleobase corresponding to the highest charge transfer from nucleobase to the phosphorene supercell. The electronic band gap for blue phosphorene is changed from indirect band gap (2.0) eV to the direct band gap of (0.77 to 1.76) eV for different nucleobase adsorption. The band gap for α is reduced and for γ is increased after adsorption of the nucleobase on phosphorene supercell. For the optical properties the absorption edges of imaginary part of the dielectric function in linearly light polarized along the X and X-Y direction shifted to lower energy when nucleobase adsorbed on phosphorene. These results suggests that phosphorene can be used as a biosensor to detect various nucleobases due to its different absorption spectra for various nucleobases.

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REFERENCES

1. J. Lee, Y. Choi, H. J. Kim, R. H. Scheicher and J. H. Cho, *J. Phys. Chem. C,* **117** , 13435 (2013).
2. H. H. Gurel and B. Salmankurt, *Mater. Res. Exp.,* **4** , 065401 (2017)
3. M. Sharma, A. Kumar and P. K. Ahluwalia, *RSC Adv.,* **6** , 60223 (2016).
4. D. C. Arriagada, *J. Phys. Chem. C,* **117** , 13435 (2018).
5. S. Kaur, A. Kumar, S. Srivastva and K. Tankeshwar, Phys. Chem. Chem. Phys. **18**,18312 (2016).
6. J. M. Soler, E. Artacho, J. D Gale, A. Garc1ia, J. Junquera, P. Ordejon, D. S. Portal, *J.Phys.:Condens. Matter,* **14** , 2745 (2002).