Energetics and Electronic Structure of Novel Hybrid Dumbbell Monolayers

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Abstract. We report three new hybrid monolayers (C_6P_4, C_6N_4 and N_6P_4) of group-IV and group-V elements in dumbbell structure using density functional theory calculations. C_6P_4, C_6N_4 possess sp^2 as well as sp^3 hybridization in their honeycomb dumbbell structure while N_6P_4 possess only the sp^3 hybridization in its non-honeycomb but dumbbell structure. The magnitude of cohesive energy of these hybrid monolayers suggests that C_6N_4 is the most favorable monolayer to be formed. We found that C_6P_4 is metallic while C_6N_4 and N_6P_4 are semiconductors. Also, we report as a representative case, the systematic structural phase transition from LHD-C to a new phosphorous allotrope which has been suggested to exists in our cohesive energy calculations. The reported monolayers join the family of two dimensional materials and may possess application in nanoelectronic devices.

INTRODUCTION

The most widely studied two dimensional (2D) allotrope of carbon is graphene [1], in which the carbon atoms are arranged in a honeycomb lattice and the atoms sharing three fold coordination with each other. Graphene possess a planar structure with sp^2 hybridization of carbon atoms. The large honeycomb dumbbell carbon (LHD-C) is formed after the adsorption of C atoms on graphene sheet which changes the coordination of some carbon atoms from sp^2 to sp^3 [2]. The structure thus consists of 3-fold as well as 4 fold coordination of carbon atoms. Since sp^3 hybridization is the favorable one for group- V elements [3, 4], so we explore the possibility of the formation of hybrid dumbbell structures based on carbon (C_6P_4 and C_6N_4), in which each of the sp^3 hybridized sites are being occupied by the group-V elements, either nitrogen or phosphorous. Also we have constructed a hybrid allotrope consisting only of the group-V elements i.e, N_6P_4 to examine whether dumbbell hybrid allotrope of group-V elements would exist or not.

COMPUTATIONAL METHOD

The first principles calculations are carried out by means of pseudopotential and numerical atomic orbitals (NAOs) basis sets, as implemented in SIESTA package [5]. The generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) exchange correlation functional is used to treat electron-electron interactions. Structural optimizations are performed using conjugate gradient method until the residual forces on each atom is less than 0.01 eV/Å. Double zeta polarization (DZP) basis sets are used to expand the Kohn-Sham orbitals with mesh cutoff energy of 450 Ry. The Brillouin zone was sampled using Monkhorst-pack scheme with a 30×30×1 mesh for

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calculations. A vacuum region of more than 20 Å is used to separate 2D monolyer structure along perpendicular direction from the periodic images.

RESULTS AND DISCUSSION

Structure and Energetics

Figure 1 depicts the crystal structure of LHD-C, C_6P_4, C_6N_4 and N_6P_4. Each of the structure consists of 10 atoms in a hexagonal unitcell. Top view as well as side view of the LHD-C, C_6P_4 and C_6N_4 are exactly the same only difference being in their bond lengths. The structure of N_6P_4 possess dumbbells (side view), however, the top view is entirely different from the dumbbell structure as it does not form hexagonal rings. This is attributed to the tendency of the nitrogen atom to form sp^3 hybridization instead of sp^2 i.e., all the atoms are 3 fold coordinated.

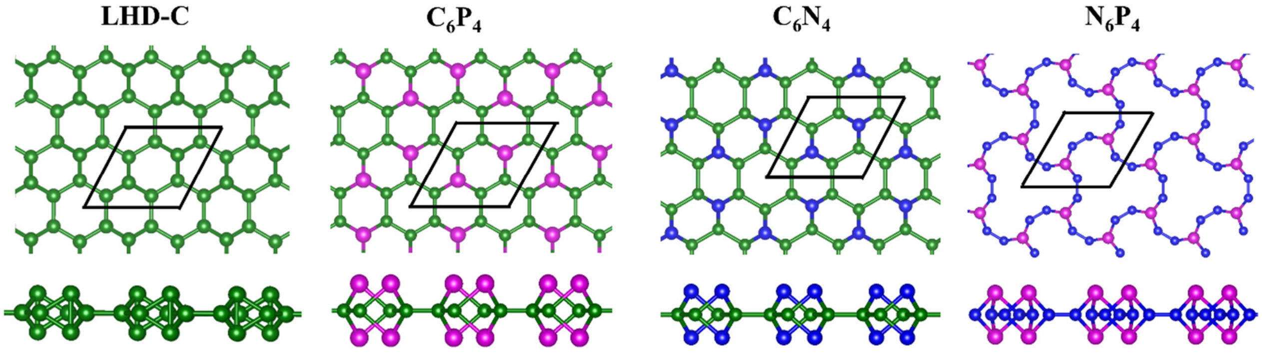

Figure 1: Top and side views of the crystal structure of (a) LHD-C, (b) C_6P_4, (c) C_6N_4 and (d) N_6P_4. Green, pink and blue color indicates carbon, phosphorous and nitrogen atoms, respectively.

In order to get an estimation about the feasibility of the formation of these hybrid structures, we calculated their cohesive energy, which is defined as the amount of energy gained when the isolated carbon, nitrogen and phosphorous atoms are arranged to make the hybrids, using the formula:

$$E_{Coh} = \frac{E_T - 6E_x - 4E_y}{N_T}$$

where, $E_x = E_c$ and $E_y = E_P$ in C_6P_4, $E_x = E_c$ and $E_y = E_N$ in C_6N_4, and $E_x = E_c$ and $E_y = E_P$ in N_6P_4. E_C / E_N / E_P represents the energy of isolated single carbon, nitrogen or phosphorous atoms. E_T is the total energy of the system, N_T is the total number of atoms in the system. The magnitude of cohesive energy comes out in the order E_{coh} (C_6N_4) > E_{coh} (C_6P_4) > E_{coh} (N_6P_4).

Table 2: Cohesive energy (E_{coh}) and bandgap (E_g) of the hybrid monolayers C_6P_4, C_6N_4 and N_6P_4.

Parameters	**C_6P_4**	**C_6N_4**	**N_6P_4**
E_{coh} (eV/atom)	7.41	8.30	6.57
E_g (eV)	0.00	1.11	1.53

Electronic Structure

The electronic band structure of the hybrid monolayers C_6P_4, C_6N_4 and N_6P_4 is shown in Figure 2. The band gap of the hybrid monolayers C_6P_4, C_6N_4 and N_6P_4 is calculated to be 0 eV, 1.11 eV and 1.53 eV, respectively (Table 1). Therefore, C_6P_4, is metallic while C_6N_4 and N_6P_4 are direct band gap semiconductors. The conduction band minimum (CBM) and valence band maximum (VBM) lies at Γ point for C_6N_4 while it lies at a point M of the Brillouin zone for N_6P_4. The major contribution to the bands in the vicinity of the Fermi level is due to the p- orbital only. We found that the states near the Fermi level are contributed mainly by the atoms at the dumbbell sites i.e. phosphorous atom in C_6P_4 and nitrogen atom in C_6N_4. However, in case of N_6P_4 the conduction band is contributed by phosphorous atoms which are present only at the dumbbell site while the valence band is mainly due to the nitrogen atom. Hence, we can say that the bands near the Fermi level are due to the sp^3 hybridized sites in all the cases.

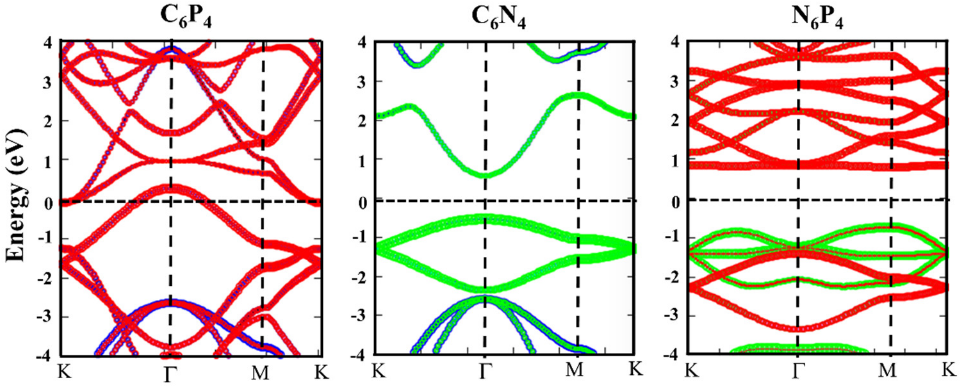

Figure 2: Electronic band structure of the hybrids C_6P_4, C_6N_4 and N_6P_4. Blue, green and red colour indicates the orbital contributions from 2p orbital of C, 2p orbital of N and 3p orbital of P, while yellow, cyan and violet colour is for 2s orbital of C, 2s orbital of N and 3s orbital of P. The Fermi energy is set at 0 eV.

Phase Transition

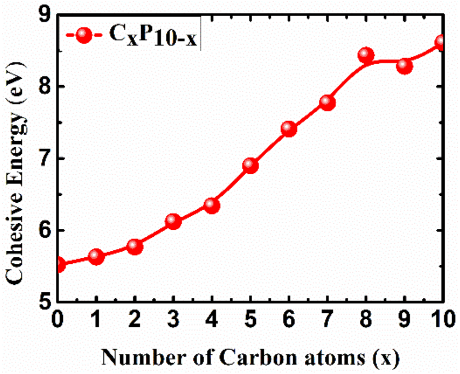

Figure 3: Cohesive energy as a function of number of carbon atoms in LHD-C.

As a representative case, we have studied the effect of replacing carbon atoms in LHD-C with phosphorous atoms one by one. Figure 3 represents the cohesive energy of all of the eleven structures. The cohesive energy decreases as we move from LHD-C with 10 carbon atoms to a new structure with 10 phosphorous atoms. The decrease in the cohesive energy may be attributed to the difference in size of the carbon phosphorous atoms and also the fact that P favors sp^3 hybridization of the atoms. Also, the cohesive energy of the new phosphorous allotrope that is formed after replacing all of the carbon atoms in LHD-C is 5.52 eV which is only 0.16 eV/atom less than that of the most stable phosphorous allotrope i.e black phosphorene [6, 7]. Hence, this there is a possibility of the formation of new phosphorous monolayer.

CONCLUSION

Based on density functional theory, we report three new and novel hybrid monolayers of group IV and group V elements in LHD structures and investigated their stability and electronic properties. The three hybrids monolayers, C_6P_4, C_6N_4 and N_6P_4, possess dumbbell structure. C_6P_4, C_6N_4 possess sp^2 as well as sp^3 hybridization in their honeycomb dumbbell structure while N_6P_4 possess only the sp^3 hybridization in its non-honeycomb but dumbbell structure. The magnitude of cohesive energy of these hybrid monolayers suggests that C_6N_4 is the most favorable monolayer to be formed. We found that C_6P_4 is metallic while C_6N_4 and N_6P_4 are semiconductors. Also, we report as a representative case, the systematic structural phase transition from LHD-C to a new phosphorous allotrope which can be formed easily as suggested by our cohesive energy calculations.

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