Dynamical stability and electronic structure of $\beta$-phosphorus carbide nano-wires

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Abstract In this work, $\beta$-phosphorus carbide 1D nano-wires (PCNWs) are investigated in the framework of density functional theory. The dynamical stability of the considered $\beta$-PCNWs at 300 K is verified using ab initio molecular dynamics calculations. According to the results on the band structure calculations, $\beta$-PCNWs can be semiconductors, semimets or metals depending on their size and form. Thus, owning to their unique shape and high tunability of electronic properties $\beta$-PCNWs may be used in optical and photovoltaic nanodevices.

Keywords: nanowires, structural stability, phosphorus carbide, 2D materials

1. Introduction

In the last decade, the number of new two-dimensional (2D) materials has been constantly growing. Advanced theoretical and novel experimental approaches make it possible to obtain hybrid 2D materials [1-4]. Recent theoretical predictions [5,6] and experimental investigations [7] have proven the existence of several allotropes of a new 2D material, phosphorus carbide (PC). Depending on its structure PC can be metallic, semi-metallic or semiconductor [5].

The predicted allotropes exhibit thermal stability and possess well tunable electronic structure [8]. In addition, the possibility of rolling of $\alpha$-PC monolayer to a PC nanotube at room temperature under compressive strain has been found has been shown [9]. Another predicted $\gamma$-allotrope of PC with an InSe-like structure has been shown to have promoted adsorption of lithium atoms, which render its application in rechargeable batteries [6]. Furthermore, $\gamma$-PC has been found as a good material for gas sensing and storage devices [10]. Very recently, $\beta$-PC has been fabricated via a novel carbon doping technique [11]. Theoretical and experimental studies have shown the existence of different $\beta$-PC phases which may have a potential for application in nanodevices [11, 12].

In this work using first-principles calculations we studied the structural stability and electronic band structure of $\beta_0$- and $\beta_1$-PC 1D nano-wires.

2. Simulation Details

The computational simulations were performed by using the Vienna ab initio simulation package (VASP) [13] within the framework of the density functional theory.

one need to evince that it cannot undergo any structural changes that lower its energy. In practice, at the first-principles level, the verification can be done using AIMD simulations.

To evince the dynamical stability of the considered structures, the ab initio molecular dynamics calculations [14] which is the most common method for low dimensional materials [15] were implemented. The structure optimization and band structure calculations the Perdew–Burke–Ernzerhof (PBE) functional with generalized gradient approximation (GGA) [16] was selected with an energy cutoff of 400 eV. All the structures were fully optimized until the forces become smaller than 0.01 eV/Å.

The optimized unicells of the considered $\beta_0$- and $\beta_1$ allotropes of PC are shown in Figure 1. The calculated lattice constants of $\beta_0$- and $\beta_1$-PC are $a = 5.050$ Å and $b = 2.915$ Å and $a =$
4.725 and \( b = 2.915 \), respectively. The results are in good agreement with the available references [4].

Figure 1. The optimized unicells of the considered (a) \( \beta_0 \)- and (b) \( \beta_1 \) allotropes of PC.

3. Simulation Results
First, we created \( \beta_0 \)- and \( \beta_1 \)-PCNWs consisting of 12 atoms and more by the rippling of \( \beta_0 \)-PC and \( \beta_1 \)-PC monolayers along their armchair (APCNW) and zigzag (ZPCNW) directions. Further, the dynamical stability of the created PCNWs is systematically checked using AIMD calculations conducted at 300 K during the period time 10 ps. It is found that the stable \( \beta_0 \)- and \( \beta_1 \)-APCNWs of the smallest/biggest size consist of 12/40 atoms. Stable \( \beta_0 \)-ZPCNWs may consist of 32 to 44 atoms, while \( \beta_1 \)-ZPCNWs consists of 24 to 44 atoms. For PCNWs found to be stable, we next calculated the band structure. Figure 2 presents the bandgap size of the considered PCNWs as a function of their size.

Figure 2. The bandgap size as a function of size of \( \beta_0 \)- and \( \beta_1 \)-APCNW and \( \beta_0 \)- and \( \beta_1 \)-ZPCNW.
Figure 3 shows the optimized atomic (upper panels) and band (lower panels) structures of $\beta_0$-APCNWs. As it is seen from Figure 3, $\beta_0$-APCNWs may have different forms such as triangle and star-like structure. Depending on the size, the $\beta_0$-APCNWs vary from a direct (wire consisting of 12 atoms) to an indirect bandgap semiconductor. According to Figure 2 with increasing the size of $\beta_0$-APCNWs from 12 atoms to 40 atoms its bandgap size decreases drastically from 1.14 eV to 0.27 eV.

The atomic and band structures of stable $\beta_1$-APCNWs are presented in Figure 4. Based on the geometry optimization results, the APCNWs are characterized by a star-like structure. The band structure calculations (Figure 2) suggest $\beta_1$-APCNWs may have a zero bandgap (wires consisting of 12 and 16 atoms), or to be a direct (wires consisting of 20 atoms) and an indirect (wires consisting of 24 to 40 atoms) bandgap semiconductors. Based on the results presented in Figure 2, the bandgap size of $\beta_1$-APCNWs is increasing by leaps from 0 eV up to 0.87 eV with increasing their size.

**Figure 3.** The atomic (the upper panel) and band (the lower panel) structures of $\beta_0$-APCNWs.

**Figure 4.** The atomic (the upper panel) and band (the lower panel) structures of $\beta_1$-APCNWs.

ZPCNWs have been found less stable than APCNWs. In case of $\beta_0$-ZPCNWs, there are only four stable configurations, which are shown in Figure 5. The $\beta_0$-ZPCNWs consisting of 32 to 40 atoms are direct bandgap semiconductors while $\beta_0$-ZPCNW consisting of 44 atoms has a zero bandgap (see Figure 5, lower panels). With increasing the size, the bandgap size of $\beta_0$-ZPCNWs decreases as it is shown in Figure 2. $\beta_0$-ZPCNWs have six stable configurations which are presented in Figure 6. The most interesting results are found for band structure of $\beta_1$-ZPCNWs. It is predicted that $\beta_1$-ZPCNW consisting of 24 atoms is metallic, $\beta_1$-ZPCNWs consisting of 28 to 40 atoms are indirect bandgap semiconductors, and $\beta_1$-ZPCNW consisting of 44 atoms is a direct bandgap semiconductor (see Figure 6, lower panels). Differently from
other PCNWs here the bandgap size of \( \beta_1 \)-ZPCNWs significantly increases with size from 0 eV to 0.97 eV (see Figure 2).

![Figure 5](image)

**Figure 5.** The atomic (the upper panel) and band (the lower panel) structures of \( \beta_0 \)-ZPCNWs.

![Figure 6](image)

**Figure 6.** The atomic (the upper panel) and band (the lower panel) structures of \( \beta_1 \)-ZPCNWs.

4. Conclusions

In conclusion, our theoretical predictions show the existence of \( \beta \)-PCNWs of different sizes and unique shapes. These \( \beta \)-PCNWs also possess existing electronic properties. Particularly, the bandgap size of \( \beta \)-PCNWs is directly depends on their size. Such tunability of the band structure suggests \( \beta \)-PCNWs as a perfect material for application in optoelectronic nanodevices.

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tor via carbon doping. Self-gated elastic minimum energy paths on battery anode boride: A study of thiazole adsorption upon BC₃N nanotube: DFT/TD-DFT investigation. Structural Chemistry 31, 1959–1967.

[3] Kaur, M., Sawhney, R. S. and Engles, D. 2017 Morphology pursuance in C20 fullerene molecular junction: ab initio implementation. Journal of Micromechanics and Molecular Physics. 02 1750007.

[4] Kochaev, A., Katin, K., Maslov, M. and Meftakhutdinov R. 2020 AA-stacked borophene-graphene bilayer with covalent bonding: Ab initio investigation of structural, electronic and elastic properties. The Journal of Physical Chemistry Letters 11(14), 5668–5673.

[5] Guan, J., Liu, D., Zhu, Z. and D. Tománek. 2016 Two-dimensional phosphorus carbide: Competition between sp² and sp³ bonding. Nano Letters 16, 3247–3252.

[6] Zhang, W., Yin, J., Zhang, P., Tang, X. and Y. Ding. 2018 Two-dimensional phosphorus carbide as a promising anode material for lithium-ion batteries. Journal of Materials Chemistry A 6, 12029–12037.

[7] Huang, X., Cai, Y., Feng, X., Tan, W. C., Hasan, D. Md. N., Chen, L., Chen, N., Wang, L., Huang, L., Duffin, T. J., Nijhuis, C. A., Zhang, Y. W., Lee, C. and Ang, K. W. 2018 Black phosphorus carbide as a tunable anisotropic plasmonic metasurface. ACS Photonics 5(8), 3116–3123.

[8] Kistanov, A. A., Korznikova, E. A., Huttula, M., and W. Cao. 2020 The interaction of two-dimensional α- and β-phosphorus carbide with environmental molecules: a DFT study. Physical Chemistry Chemical Physics 22, 11307-11313.

[9] Shcherbinin, S. A., Zhou, K., Dmitriev, S. V., Korznikova, E. A., Davletshin, A. R. and Kistanov A. A. 2020 Two-dimensional black phosphorus carbide: rippling and formation of nanotubes. The Journal of Physical Chemistry C 124(18), 10235–10243.

[10] Kistanov, A. A. 2020 The first-principles study of the adsorption of NH₃, NO, and NO₂ gas molecules on InSe-like phosphorus carbide. New Journal of Chemistry 44, 9377-9381.

[11] Tan, W. C., Cai, Y., Ng, R. J., Huang, L., Feng, X., Zhang, G., Zhang, Y. W., Nijhuis, C. A., Liu, X., Ang, K. W. 2017 Few-layer black phosphorus carbide field-effect transistor via carbon doping. Advanced Materials 29, 1700503.

[12] Li, F., Liu, X., Wang, J., Zhang, X., Yang, B., Qu, Y. and Zhao M. 2017 A promising alkali-metal ion battery anode material: 2D metallic phosphorus carbide (β₀-PC). Electrochimica Acta 258, 582–590.

[13] Kresse G. and Furthmüller J. 1996 Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Physical Review B 54(16), 11169-11186.

[14] Henkelman, G., Uberuaga, B. P. and Jonsson H. 2000 A climbing image nudged elastic band method for finding saddle points and minimum energy paths. The Journal of Chemical Physics. 113, 9901.

[15] Malyi, O. I., Sopiza, K. V. and Persson C. 2019 Energy, phonon, and dynamic stability criteria of two-dimensional materials. ACS Applied Materials and Interfaces. 11(28), 24876–24884.

[16] Perdew, J. P., Burke, K. and Ernzerhof, M. 1996 Generalized gradient approximation made simple. Physical Review Letters 77(18), 3865-3868.