1. INTRODUCTION

Modern experimental techniques developed in the past decade, such as molecular beam epitaxy,12 atomic layer deposition,3,4 pulsed laser deposition,5,6 and magnetron sputtering,7,8 have contributed to a giant leap in the synthesis of two-dimensional (2D) materials, as well as the production of technological devices based on these materials.8−11 For example, the forefather of 2D materials, graphene, was obtained using mechanical exfoliation.1,12 Another classical 2D material, phosphorene, was fabricated via liquid-phase exfoliation13 and pulsed laser exfoliation.5 One should not underestimate the contribution of atomistic simulations in the investigations of 2D materials. For instance, first-principles calculations predicted the existence of group V elements, arsenene and antimonene,14,15 for the first time.

The above-mentioned technologies have rendered 2D materials no longer a vision of the future but materials of the present day, and have promoted an extensive study of their structure, properties and applications. However, contemporary knowledge on 2D materials concludes that each 2D monolayer possesses some inherent disadvantageous properties. Despite its unique chemical stability, high mechanical durability, and excellent carrier mobility, graphene has no intrinsic band gap.16−20 Transition metal dichalcogenides21,22 possess sizable and tunable band gaps, but they present several disadvantages, depending on their fabrication methods, such as a relatively low carrier mobility, large volume expansion, and phase conversion.23 A recently predicted and isolated group of materials such as phosphorene, arsenene, and antimonene have extraordinary properties,14,24 including remarkable charge mobility and wide and highly tunable band gaps (0.3−2 eV). However, these materials are chemically active and structurally unstable in standard ambient conditions.25−27

As a new class of materials, hybridized composites that combine the advantages and counteract the disadvantages of their constituent compounds are currently emerging in the spotlight.35−38 These materials can exist as heterostructures consisting of several layered 2D materials,13,24−26 such as graphene/phosphorene, graphene/indium selenide, boron nitride/phosphorene, or 2D layers consisting of atoms of different elements.42−44 It has been demonstrated that heterostructures formed by 2D materials, which are unstable in standard ambient conditions, such as phosphorene, and 2D materials, which are stable, such as graphene, are characterized by improved stabilities.37,38,45,46 Very recently, a stable
allotrope of phosphorus carbide (PC), a 2D monolayer consisting of carbon and phosphorus atoms, has been discovered.\textsuperscript{47−50} It has a wide band gap reaching up to 2.65 eV,\textsuperscript{48} robust superconducting behavior even under tensile strain,\textsuperscript{51} a small effective mass, and extra-high carrier mobility.\textsuperscript{52}

It is well-known that the different properties of 2D materials can be modified by strain engineering.\textsuperscript{53−57} For phosphorene, it has been shown that in-plane strain transition and affects its charge carrier mobility.\textsuperscript{56,57} The strong spatial dependence of the electronic structure upon the rippling of phosphorene along its periodic line profile, which may be used for modulating the injection and confinement of its carriers, has been established both theoretically\textsuperscript{58} and experimentally.\textsuperscript{59} However, there have been no similar systematic studies conducted on the rippling of a PC monolayer under a significant out-of-plane deformation.

Graphene and phosphorene nanotubes are currently the subjects of intensive research as base materials for a large variety of technological applications from sensing devices to active optoelectronic elements.\textsuperscript{60,61} For example, phosphorene nanotubes are direct band gap semiconductors and their electronic properties can be modified by strain or electric field engineering.\textsuperscript{62} Meanwhile, graphene nanotubes are common additives to polymer hosts for the manufacturing of advanced composite materials\textsuperscript{63,64} and as electrode materials for batteries and supercapacitors.\textsuperscript{65} Carbon nanotube bundles are promising for shock and vibration protection applications.\textsuperscript{66−71} However, PC nanotubes (PCNTs) are much less studied.

This study systematically investigated the evolution of the atomic structure, the electronic and mechanical properties of a rippled α-PC monolayer under large compressive strain. Based on the work,\textsuperscript{56} where layered PC, similar to black phosphorene, was found to be soft when strained along its armchair direction compared with a zigzag direction, our investigation focuses on the armchair rippled α-PC monolayer due to its high flexibility. After discovering that the α-PC monolayer is able to form nanotubes under large compressive strains applied along its armchair direction, PCNTs are also studied with their thermal stability, atomic structure and electronic and mechanical properties analyzed.

2. COMPUTATIONAL METHODS

This work is based on the spin-polarized density-functional theory (DFT) as implemented in the VASP code.\textsuperscript{72} The Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional under the generalized gradient approximation (GGA)\textsuperscript{73} is used for the geometry optimization and electronic structure calculations. Since in the GGA PBE approach the fundamental band gap is usually underestimated, the HSE06\textsuperscript{74} hybrid exchange-correlation functional is adopted to obtain more accurate band structures. The cutoff energy for plane waves is set at 450 eV. The geometries of all structures are fully optimized until the total energy and all forces on atoms converge to less than $10^{-8}$ eV and 0.01 eV/Å, respectively. The vacuum depth of 15 Å is introduced for all the structures, for both monolayers and nanotubes, to avoid artificial interaction in a supercell. The periodic boundary conditions are applied for the two in-plane transverse directions. The considered supercell of an α-PC monolayer is composed of $3 \times 4$ unit cells (12 C and 12 P atoms). The study of α-PC nanotubes (PCNTs) commences with nanotubes of the smallest possible size (4 C atoms and 4 P atoms). In this work, a PCNT consisting of 40 atoms (PCNT40) is considered, to compromise for the computational demand.

The rippled structures of an α-PC monolayer are created by applying a compressive strain along the armchair directions. The compressive strain is defined as

$$\varepsilon = \frac{l - l_0}{l_0}$$

where $l$ and $l_0$ are the lattice constants of the strained and initial supercells, respectively. The compression is performed in steps. After each step, the structure is fully relaxed through the technique of energy minimization. Because of the period boundary conditions with a fixed period applied laterally, along the armchair direction, the lattice spacing along the zigzag direction remains unchanged.

The Young’s modulus of the considered PCNTs is calculated with the aid of the energy-strain relation.\textsuperscript{75,76} A set of positive and negative uniaxial strains $\varepsilon$ are applied to the initially unstrained structure along the zigzag direction. For each case considered, the corresponding energy values are calculated. The obtained set of energy values corresponding to each applied strain is then used for a polynomial fitting of energy potential $U(\varepsilon)$. The Young’s modulus is computed by

$$E = \frac{1}{V} \left( \frac{\partial U(\varepsilon)}{\partial \varepsilon} \right)_{\varepsilon=0}$$

where $V$ is the volume of the unit cell of the considered PCNT. Here, it is assumed that $V = 2\pi R l$, where $R$ is the mean radius of the nanotube, while $l$ is the interlayer distance of the α-PC monolayer ($l = 4.93$ Å, as obtained from DFT calculations). As a consequence of the applied uniaxial tensile strain $\varepsilon$, a negative radial strain $\varepsilon_r$ is obtained. The Poisson’s ratio $\nu$ is calculated by a linear fitting of $\varepsilon$ versus $\varepsilon_r$ as

$$\nu = -\frac{\varepsilon_r}{\varepsilon}$$

The Young’s modulus along the zigzag direction for rippled α-PC under the compressive strain applied along the armchair direction is also calculated. It should be noted that internal stresses affect the calculation of the Young’s modulus of an elastic body.\textsuperscript{67} However, the elastic modulus of α-PC in the armchair direction is 1 order of magnitude smaller than that in the zigzag direction and thus, a compression along the armchair direction produces rather small stresses. Therefore, internal stresses can be neglect when calculating the Young’s modulus of α-PC along the stiff zigzag direction using the energy-strain relation.

Ab initio molecular dynamics (AIMD) calculations\textsuperscript{77} are conducted at 300 K to verify the thermal stability of PCNTs. The simulation lasts for 10 ps with a time step of 1.0 fs and the temperature is controlled by a Nose–Hoover thermostat. It should be noted that in AIMD calculations the considered unit cell of PCNT40 is repeated three times in the axial direction to show structural evolution of PCNT40 (the total number of atoms is 120) in this direction as well.

3. RESULTS AND DISCUSSION

3.1. Electronic Structure and Mechanical Properties of an α-PC Monolayer. An α-PC monolayer is considered as it was found to be one of the stable allotropes of PC.\textsuperscript{48,78} Moreover, the α-PC monolayer was predicted to possess distinguishable features\textsuperscript{47−49,52} such as a wide band gap and a
high Young’s modulus. The geometry, electronic structure, and Young’s modulus of the α-PC monolayer are investigated. The considered α-PC structure and its unit cell (bounded by the dashed line) are presented in Figure 1a. The obtained relaxed lattice constants \(a = 8.56 \, \text{Å} \) and \(b = 2.92 \, \text{Å} \) are in good agreement with the previously reported results.\(^{47-49}\) Our HSE06 calculations determine the band gap to be 1.32 eV. Our PBE GGA calculations predict a qualitatively similar band structure but slightly underestimate the band gap, which is 0.76 eV in that case. Both values match the reference results obtained by the HSE06\(^{46}\) and PBE GGA\(^{48,49}\) functionals.

To avoid the high computational cost of hybrid functional calculations, we report the results based on the PBE GGA approach. The Young’s moduli of the α-PC monolayer along its armchair and zigzag directions is found to be 27.08 and 348.69 GPa, respectively. The obtained Young’s moduli are smaller than those of graphene,\(^79\) but significantly higher than those of phosphorene.\(^80\) Interestingly, the α-PC monolayer is found to possess a mechanical strength similar to that of a γ-PC monolayer and superior to that of phosphorene.\(^50\) The shear modulus of the α-PC monolayer reaches up to 81.80 GPa and the Poisson’s ratios are 0.25 and 0.019 for tension along the armchair and the zigzag direction, respectively.

### 3.2. Atomic Structure and Electronic and Mechanical Properties of Rippled α-PC.

To examine the extreme effects of strain engineering on the rippling of an α-PC monolayer and the possibility of formation of nanotubes as a result of compression, compressive strain is applied along its armchair direction (along which the material is more flexible). Figure S1 shows the atomic (upper panel) and band (lower panel) structures of the rippled α-PC monolayer under compressive strain ranging from 0 to 48%. The correlation between the band gap size and the applied strain is depicted in Figure 2a. First, for the compressive strain ranging from 0 to 11%, the band gap size slightly decreases from 0.76 to 0.47 eV. At the same time, there is no perceptible change to the structure of the rippled α-PC monolayer within the range of the applied strains. Further compression (to 16%) causes a drastic decrease of the band gap size to 0.22 eV. Then, for the compressive strain values of 22 and 28%, the band gap size jumps to 0.54 and 0.56 eV, respectively, and finally decreases linearly to 0.43 eV as the compressive strain reaches \(\sim 48\%\). It should be noted that an indirect–direct band gap transition occurs in the α-PC monolayer when the compressive strain is between 6 and 11%. Meanwhile, at the compressive strain higher than 11%, a direct band gap is observed and the valence band maximum and conduction bands minimum shift from the Γ to the Y point.

Since rippling usually changes the work function of 2D materials,\(^81,82\) the work function of the rippled α-PC monolayer is examined. Figure 2b shows the work function of the α-PC monolayer as a function of the applied compressive strain. The work function of the unstrained monolayered α-PC is 4.77 eV, which is higher than that of graphene (4.50 eV)\(^83\) and lower than that of phosphorene (5.04–5.16 eV).\(^84\) Moreover, the work function of the α-PC monolayer is found to have a general tendency to increase with the compressive strain but experience a sharp drop when the strain ranges from 11 to 16%. The observed increase of the work function of α-PC may be attributed to the role of the stress accumulated upon the increase of the strain and stretching of the atomic bonds which leads to the shift of the valence band maximum (see Figure S1).\(^85\) A similar linear increase in the work function caused by in-plane strain has recently been reported for MoS\(_2\) nanosheets.\(^86\)

According to Figure 2c, the Young’s modulus of the rippled α-PC monolayer significantly decreases from 348.69 to 290.4 GPa as the compressive strain increases from 0 to 16%. A drastic plummet of the Young’s modulus occurs at the compressive strain of 16% at the moment of the significant stress accumulation. The subsequent increase of the compressive strain to 32% induces a rapid increase of the Young’s modulus up to 341.43 GPa. As the compressive strain increases from 32 to 48%, the Young’s modulus slightly decreases to 334.33 GPa.

The analysis shows that there is an accumulation of the stress upon the increase of the strain to \(\sim 11\%\), while as the
compressive stain reaches \( \sim 16\% \), a stress relaxation occurs, which results in a decrease of the band gap size, work function, and Young's modulus. A further increase in the compressive strain, after the release of stress, results in a sharp increase of...
the band gap size, work function, and Young’s modulus of rippled α-PC. This can be explained by a specific hinge-like structure of α-PC in its armchair direction (Figure 1c, lower panel), which allows α-PC to withstand large compressive strains without breaking, similar to phosphorene.36,38 To demonstrate this feature, the following structural parameters of the rippled α-PC monolayer during the compression deformation are tracked: the bond lengths P−P1 and P−P2 connecting the hinges, the bond lengths of the hinges C−C1, C−C2, C−P1, and C−P2, and the hinge angles CPC1, CPC2, PCC1, PCC2, PPC1, and PPC2, as shown in the lower panel of Figure 3a. The variations of the bond lengths and angles are presented in Figure 3b and c, respectively.

Indeed, for a compressive strain up to 16%, there are no remarkable changes in the structural parameters except for a slight elongation of the P−P1 and P−P2 bonds and a slight decrease of the PPC1 and PPC2 angles. Noticeable changes of the structural parameters begin at a compressive strain of 4p s( Movie 1 in the Supporting Information (SI)). The oscillation of the P−P1 and P−P2 bonds and a slight elongation of the C−C1 and C−C2 bonds (Figure 3b), (ii) a decrease of the PCC1 angle, and (iii) a decrease of the PPC2 angle and an increase of the PPC1 angle (Figure 3c). The observed discrepancies of the angles indicate that the structure folds like a hinge upon reaching a central level of compressive strain (16%), which facilitates the relaxation of the accumulated stress. When the compressive strain exceeds 50%, the breaking of two P−P bonds at the base of the structure and the formation of a single P−P bond occur with the restructuration of rippled α-PC to form a nanotube-like structure. Our AIMD calculations show that transformation of α-PC from the rippled structure into the nanotube-like structure under a compressive strain of ~50% occurs within ~4 ps (Movie 1 in the Supporting Information (SI)). The nanotube is unstable over a long period of time because in this case, however, from this simulation, the possibility of rolling the rippled α-PC to a nanotube is revealed. Previously, nanotubes formed by strain-induced rolling have been predicted experimentally for InxGa1−xAs-GaAs membranes.87

3.3. Atomic Structure and Electronic and Mechanical Properties of α-PC Nanotubes. Since the formation of α-PC nanotubes by the rippling of an α-PC monolayer under large compressive strains is found to be possible, the atomic configurations and the electronic and mechanical properties of these nanotubes are investigated. To determine the smallest size of a stable α-PC nanotube (PCNT), AIMD simulations are conducted for PCNTs consisting of 8 (PCNT8), 16 (PCNT16), 24 (PCNT24), 32 (PCNT32), and 40 (PCNT40) atoms. Movie 2 in SI shows the AIMD results for PCNT40, while its atomic structure is shown in Figure 4a. Meanwhile, the atomic structures of PCNT24 and PCNT32 are shown in Figure S2. According to our calculations, PCNT24, PCNT32, and PCNT40 are direct band gap semiconductors with band gap sizes of 0.29, 0.57, and 0.67 eV, respectively. The Young’s moduli of PCNT24, PCNT32, and PCNT40 along their nanotube axes are 315.87, 328.20, and 333.92 GPa. On the other hand, their Poisson’s ratios are 0.20, 0.23, and 0.28, respectively. The calculated cohesive energies of PCNT24, PCNT32, and PCNT40 are −6.695, −6.741, and −6.743 eV/atom, respectively, suggesting that the stability of the nanotube slightly increases with its size. Our prediction also suggests that the PCNTs have a Young’s modulus about three times less than that of carbon nanotubes88,89 but about two times higher than that of phosphorene nanotubes.90,91 Meanwhile, the Poisson ratio of the PCNTs is comparable to that of carbon nanotubes.92

Figure 4b presents the band gap size of PCNT40 as a function of the strain, both compressive and tensile, applied along its nanotube axis (Figure 4a, upper panel). Here, we shall only discuss the results for PCNT40 as PCNT24 and PCNT32 display similar behaviors (Figure S2 and SI for more details). The band gap of PCNT40 decreases rapidly from 0.67 to 0 eV...
as the compressive strain increases from 0 to 9%. Meanwhile, at a compressive strain of 3%, the conduction band minimum shifts from between the F and Q points to a Γ point (Figure S3), signifying a direct-to-indirect band gap transition. Furthermore, at a compressive strain of 9% and beyond, the band gap disappears completely, affirming a semiconductor-to-metal transition. An increase in the tensile strain from 0 to 9% leads to an increase of the band gap size from 0.67 to 0.95 eV (Figure 4b). A rapid decrease of the band gap size is observed when the tensile strain is increased from 9% to 20%. Increasing the tensile strain from 20 to 30% results in the termination of the band gap and a remarkable structure deformation. In particular, a drastic decrease of the PCC1 and PCC2 angles, an increase of the CPC1 and CPC2 angles, as well as a significant elongation of the CP1 and CP2 bonds are observed. Further increasing of a tensile strain would cause nanotube to break.

To understand the changes in the band structure of PCNT40 induced by strain, its structural parameters are analyzed. The following structural parameters (Figure 4a, lower panel) are tracked: (i) the bond lengths of PP1 and PP2 connecting the hinges, (ii) the bond lengths of the hinges CC1, CC2, CP1, and CP2, and (iii) the hinge angles CPC1, CPC2, PCC1, PCC2, PPC1, and PPC2. The variation of the bond lengths and angles are presented in Figure 4c and d, respectively. As shown, the band gap size correlates with the bond lengths and angles. Under an increasing compressive strain from 0 to 6%, the band gap size slowly decreases. In addition, the following minor changes under these strains are observed: the bonds PP1 and PP2 are slightly elongated and the bonds CC1 and CC2 remain almost unchanged, while the bond angles PCC1, PCC2, PPC1, and PPC2 linearly increase. When the compressive strain is increased from 6 to 9%, the following significant changes in the structural parameters take place: the lengths of the PP1 and PP2 bonds drastically increase and the CC1 and CC2 bonds are also elongated noticeably, while the PCC1 angle decreases and the PPC1 and PPC2 angles significantly increase. In addition, there is an almost linear positive correlation between the tensile strain and the band gap size, the bond lengths CP1 and CP2, and the bond angles CPC1 and CPC2. On the other hand, the tensile strain exhibits a negative linear correlation with the bond lengths PP1, PP2, CC1, and CC2 as well as the bond angles PCC1, PCC2, PPC1, and PPC2. It can be concluded that direct–indirect and semiconductor-to-metal transitions in PCNT40 occur mainly due to the transformation of the band lengths and angles.

To further understand the effects of strain on the electronic structure of PCNT40, the electron localization function (ELF) for PCNT40 under different strains is calculated. For PCNT40 under the compressive strain of 9% and PCNT40 under the tensile strain of 20%, the isosurface value of 0.65 is adopted in Figure 5a–c. For the same structures in Figure 5d–f, the value of the ELF maps (between 0 and 1) reflects the degree of charge localization in the real space, where 0 represents a free electronic state while 1 represents a perfect localization. As shown in Figure 5b and e, the electrons are packed together at C–P bonds (the red circle) and slightly delocalized at P–P (the black circle) bonds. As indicated in Figure 5a and d, the compression strain of 9% leads to an increase of electrons at P atoms and their localization at C–P bonds (the red circle) while at P–P bonds (the black circle) electrons are almost delocalized, which suggests the nearly broken P–P bonds. Under the tensile strain of 20% (Figure 5c and f), the electrons at P–P bonds exhibit a more highly concentrated distribution while at C–P bonds their localization decreases, which indicates a strong covalent chemical bonding between P atoms.

4. CONCLUSIONS

By applying first-principles simulations, we examined and explained the modification of the electronic and mechanical properties of α-PC upon rippling under a large compressive strain along the armchair direction. It was found that the Young’s modulus of rippled α-PC varies from 290.41 to 348.69 GPa under different compressive strains. Rippling also causes an indirect–direct band gap transition in α-PC and modifies its work function. In addition, the possibility of restructuring of α-PC into a nanotube-like structure under extreme compressive strains was revealed. α-PC nanotubes of different sizes were subsequently studied, and the smallest diameter for an α-PC nanotube to be stable at 300 K were evaluated. The electronic and mechanical properties of stable α-PC nanotubes of different diameters were also investigated. The Poisson’s ratio of α-PC nanotubes was not inferior to that of phosphorene nanotubes, while their Young’s modulus was found to exceed that of phosphorene nanotubes. The investigated α-PC nanotubes possess a highly tunable band gap under compressive and tensile strains applied along the nanotube axis. Moreover, through strain engineering, it is possible to achieve a semiconductor-to-metal transition in α-PC nanotubes or significantly enlarge their band gap size. Therefore, our work suggests rippling as an effective method to tune the mechanical and electronic properties of an α-PC monolayer. We also show the possibility of PCNTs fabrication by rippling of a α-PC monolayer under extreme compressive strains. Due to their newly found extraordinary properties, PCNTs may eventually replace phosphorene and graphene nanotubes in the design of nanodevices and find application in straintronic, optical, and photovoltaic devices.
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