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ABSTRACT

We report on mechanical properties of blue phosphorus nanotubes (BluePNTs) from systematic molecular dynamics simulations, adopting a Stillinger-Weber potential with parameters determined by fitting to energetic and structural data from first-principles calculations. Our results corroborate the previously reported bending poison effect and size-dependent buckling behaviors. Under axial compression, current simulations predict a shell-to-column buckling mode transition for BluePNTs with increasing aspect ratios; further compression of BluePNTs with large aspect ratios results in a column-to-shell buckling mode transition. Associated critical buckling strains can be described by the continuum mechanics theory. We also simulated buckling behavior of black phosphorus nanotubes (BlackPNTs) and found that the buckling modes of BluePNTs exhibit much less chirality dependence compared to BlackPNTs, stemming from subtle structural differences between these two closely related yet distinct systems. The present results offer insights into key structural and mechanical properties of BluePNTs for fundamental understanding and potential applications of this relatively new member of the large and diverse nanotube family of materials.

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I. INTRODUCTION

The discovery of graphene has opened a new research field for exploring exotic properties of two-dimensional (2D) materials.^{1,2} However, the lack of a finite electronic bandgap in graphene has hindered its applications in semiconducting devices.³ Transition metal dichalcogenides like MoS₂ have been studied for better performances in transistors.^{4,5} It was recently shown that black phosphorus, another elemental 2D crystal, also exhibits good semiconducting performances,^{6,7} but the highly anisotropic properties of black phosphorus impede its applications.^{8,9} Another phosphorus allotrope, namely, the blue phosphorus, was later found to exhibit more desirable semiconducting features following first-principles calculations.^{10,11} Structurally, this distinct phosphorus allotrope is much less anisotropic compared to black phosphorus. It is, therefore, of considerable interest to further explore

mechanical properties of this new 2D material to assess its potential for electromechanical applications.

It is noted that prior to the peeling of atomic-thin graphene sheets, their rolled-up form of carbon nanotubes (CNTs) was synthesized and shown to exhibit outstanding mechanical and electronic properties.¹² The hollow tubular structure makes CNTs highly functional and their deformation patterns distinct from those of one-dimensional nanowires. For example, CNTs can resist buckle under larger deformation without losing their structural integrity. The first buckling phenomenon was revealed by Iijima *et al.* using high resolution electron microscopy,¹³ and this behavior was later reproduced by molecular dynamics (MD) simulations. It was found that the continuum mechanics theory is able to capture the underlying mechanism although structures at nanoscale are no longer in the continuum realm.¹⁴ Following these pioneering studies, further experimental and simulation works uncovered

complex phenomena and deep insights into buckling mechanics,^{15–20} revealing crucial knowledge on the effects of tube size, wall thickness, and chirality, as well as temperature and loading conditions. Similar to graphene, blue phosphorus can also be rolled into tubes to form blue phosphorus nanotubes (BluePNTs). This material is, however, different from CNTs in that its bond strength is much weaker than that of sp^2 type carbon bonds and that its structure is not truly planar but has a slightly out-of-plane deformation character. A crucial task is to establish mechanical responses of BluePNTs under strain and also determine whether traditional mechanics theories are still applicable to describe this promising nanoscale material.

In this work, we report on systematic molecular dynamics (MD) simulations to study the structural and mechanical properties of blue phosphorus and its 1D derivative BluePNTs. We developed a Stillinger-Weber (SW) interatomic potential by fitting to data from first-principles calculations. The SW potential provides a good description of several key known properties, such as the bending poison effect and its chirality dependency. Our results show that blue phosphorus is less anisotropic in structural and mechanical properties compared to black phosphorus that has a more pronounced puckering character. For BluePNTs, the binding energy decreases with tube diameter, similar to the case for CNTs. Analysis shows that the buckling mode of BluePNTs transitions from shell buckling to column buckling when the aspect ratio of the tube increases, consistent with existing buckling theory for CNTs. For BluePNTs with large aspect ratios, another transition from column buckling to shell buckling is observed at further increased strains. The critical strains for both buckling modes are consistent with trends predicted by the continuum mechanics theory. Comparison with black phosphorus nanotubes (BlackPNTs) indicates that buckling modes of BluePNTs are less chirality dependent, due to their weaker puckering character. The present results establish key benchmarks for understanding mechanical responses of BluePNTs under axial compression, which play crucial roles in potential structural and mechanical applications.

II. METHODS

First-principles calculations were conducted to obtain energetic and structural details of blue phosphorus for the ensuing development of the Stillinger-Weber interatomic potential, and these calculations were performed using the VASP package.²¹ The generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form^{22,23} for the exchange and correlation potential together with the projected-augmented wave (PAW) method was adopted. An energy cutoff of 400 eV was chosen for the planewave basis, and the structures were fully relaxed until the forces on all atoms were less than 0.01 eV/Å. The fully relaxed blue phosphorus unit cell of 4 atoms has the dimensions of $5.67 \times 3.28 \text{ Å}^2$, with an out-of-plane buckling height of 1.24 Å, which are in good agreement with previously reported results.¹¹ After structural optimization, the unit cell was subjected to uniaxial strain in armchair or zigzag direction to obtain strain energy and corresponding structural parameters, as shown in Fig. 1. Here, the strain energy is defined as the change of total

energy per atom compared to that at zero strain, i.e., $\Delta E = (E - E_0)/4$, where E_0 is the total energy of the unit cell after energy minimization and E is the total energy of the system under strain. These results were then used for the SW potential parameter fitting as described below.

Molecular dynamics simulations were performed using the LAMMPS package.²⁴ The SW potential²⁵ defined below was used to describe the interatomic interactions in blue phosphorus,

$$E = \sum_i \sum_{j>i} \phi_2(r_{ij}) + \sum_i \sum_{j \neq i} \sum_{k>j} \phi_3(r_{ij}, r_{ik}, \theta_{ijk}), \quad (1)$$

where

$$\phi_2(r_{ij}) = A_{ij} \epsilon_{ij} \left[B_{ij} \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{p_{ij}} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{q_{ij}} \right] \exp \left(\frac{\sigma_{ij}}{r_{ij} - a_{ij} \sigma_{ij}} \right) \quad (2)$$

and

$$\begin{aligned} \phi_3(r_{ij}, r_{ik}, \theta_{ijk}) = & \lambda_{ijk} \epsilon_{ijk} [\cos \theta_{ijk} - \cos \theta_{0ijk}]^2 \\ & \times \exp \left(\frac{\gamma_{ij} \sigma_{ij}}{r_{ij} - a_{ij} \sigma_{ij}} \right) \exp \left(\frac{\gamma_{ik} \sigma_{ik}}{r_{ik} - a_{ik} \sigma_{ik}} \right). \end{aligned} \quad (3)$$

Equation (2) describes two-body bond stretching interactions (depending on r_{ij}) and Eq. (3) describes three-body bond angle interactions (i.e., a function of θ_{ijk}). Among the parameters used in Eqs. (2) and (3), A_{ij} is the two-body potential well depth, B_{ij} and a_{ij} are unitless geometric parameters, and σ_{ij} and θ_{0ijk} are geometric parameters that relate to the energy minimum distance and bond angle energy minimum. From experimental and first-principles data,^{10,11} it was determined that $\cos \theta_{0ijk} = -0.05318$. λ_{ijk} is the three-body potential well depth. Other parameters used in this work include $\epsilon_{ij} = 1$, $p_{ij} = 4$, $q_{ij} = 0$, and $\gamma_{ij} = 1.0$. Parameters of A_{ij} , B_{ij} , σ_{ij} , a_{ij} , and λ_{ijk} were carefully fitted from structural features of the 2D blue phosphorus and its strain energy-strain relations. These parameters are scanned over wide ranges to calculate key features (including strain energy at various strain levels, elastic modulus, lattice geometries, etc.) of BlueP. By comparing results obtained from first-principles calculations and those from the SW potential, the set of parameters that produces the smallest overall error is chosen. The best fits are shown in Figs. 1(a) and 1(b), and the corresponding parameters are $A_{ij} = 8.4 \text{ eV}$, $B_{ij} = 33.5$, $\sigma_{ij} = 0.822 \text{ Å}$, $a_{ij} = 3.44$, and $\lambda_{ijk} = 58.7 \text{ eV}$. The obtained unit cell with these parameters is $5.676 \times 3.277 \text{ Å}^2$, and the buckling height is 1.232 Å, the 2D elastic modulus in x and y directions are 68.8 N/m and 62.9 N/m, respectively. These results are all very close to the data produced by first-principles calculations and those reported in the literature.^{10,11,26,27} A copy of the potential file used in LAMMPS calculations are included in the [supplementary material](#).

BluePNTs were obtained by rolling 2D blue phosphorus sheets into 1D nanotubes along armchair or zigzag directions, and the length-to-diameter ratio (i.e., aspect ratio, L/d) considered in this work ranges from 5 to 30, with periodic boundary conditions applied along the axial direction. In this paper, armchair nanotubes

FIG. 1. Strain energy along the (a) armchair or (b) zigzag direction of a 2D blue phosphorus sheet. Black solid symbols are from first-principles calculations, while blue and red hollow symbols are results from the fitted SW potential. The corresponding structural model from the SW potential calculations is shown in (c), where the out of plane buckled structure with a height of 1.24 Å is clearly seen, and the red dashed rectangle denotes the unit cell used in both first-principles and MD calculations.

are denoted by index (m, m) and zigzag nanotubes are denoted by $(n, 0)$; here, m and n are integers, similar to those defined in other nanotubes such as carbon.²⁸ The structures were first relaxed using the conjugated-gradient method for further compression simulations. Axial strains were applied to the simulation box along the BluePNT axial direction at a rate of 0.1% per 2 ps, while the time step used in the simulation was 1 fs. To minimize thermal fluctuation effects, the simulations were kept at a low temperature of 5 K using the Nose-Hoover thermostat.²⁹ This choice of low temperature is conventionally used in studies reported in the literature for studying buckling behavior of nanotubes.^{13,20,30–32} This is because the sudden drop of strain energy in nanotubes during compression is a key indication of buckling occurrence, but the drop is relatively small and could be masked by the thermal energy if simulated at higher temperature. Structural responses were then tracked to

uncover the buckling characters of BluePNTs. For comparison, nanotubes from black phosphorus were also studied using the same approach with the SW parameters obtained from the literature.³³

III. RESULTS AND DISCUSSION

We present in Fig. 2 typical energetic and structural data of BluePNTs. Due to the nonplanar nature of 2D blue phosphorus, BluePNTs exhibit intrinsic buckled structures on tube surfaces, consistent with previously reported results.¹¹ The strain energy (or curvature energy, defined as E_c) increases with reducing tube diameter, which is consistent with results for nanotubes in general, because a smaller diameter means a higher curving strain. Interestingly, we also observed the bending poison effect³⁴ in BluePNTs, as shown in Figs. 2(b) and 2(d), where it is seen that

FIG. 2. (a) and (c) Curvature energy and (b) and (d) axial lattice constants of BluePNTs from SW potential calculations. Representative nanotube structures are shown in the insets of (b) and (d).

axial lattice parameters of the armchair and zigzag BluePNTs decrease and increase, respectively, with an increasing diameter. The stress-strain relationships for some selected BluePNTs are shown in Fig. 3. It is seen that all BluePNTs exhibit linear stress-strain relations within a small strain range (say, between -2% and 2% , with negative strain indicating compression), and Young's modulus (Y) can then be extracted by a linear fitting to these curves and the results are shown in Fig. 3(b). It is noted that the stress obtained here is defined as force divided by the cross-sectional area (i.e., BluePNTs are considered as solid cylinder); therefore, Young's modulus obtained for BluePNTs decreases with increasing diameter. If the stresses are calculated as forces divided by πDh , where D is the diameter and h is the BluePNT wall thickness (i.e., BluePNTs are treated as hollow cylinders), then Young's modulus increases with BluePNT diameters. This is because smaller PNTs pose larger intrinsic curvature energy and, therefore, compromise their mechanical strength.³⁵ Our results are consistent with those observed in BlackPNTs as reported by Chen *et al.*³⁶ The only difference is that Young's modulus of BlackPNTs is more chirality dependent due to the anisotropic nature of black phosphorus. As will be discussed later, this feature is also closely related to the buckling characteristics of BlackPNTs. At larger tensile strains, the stress-strain relations become nonlinear and drop suddenly when fracture occurs. Owing to the larger curvature energy for small BluePNTs, it is also found that the fracture strain of BluePNTs slightly increases with their diameter, as can be seen in Fig. 3(d). The fracture stress shown in Fig. 3(c) exhibits less sensitivity to diameters, mainly due to the definition of the stress used here. When compressed to critical strains, the stress-strain relation also changes dramatically, and these phenomena are closely related to the buckling behavior, which we will discuss below. These results reproduce some key known properties of blue phosphorus,^{10,11,26,27} thus indicating the reliability of the potential parameters developed in the present work. We also note that for extremely small nanotubes, strong hybridization between bonding types may lead to abnormal physical behaviors and nonlinear elastic and plastic properties,³⁷ which is beyond the capability of SW potentials in general. The users are, therefore, advised to use the potential with caution when studying cases involving extreme strains. Below,

we proceed to take this approach to examine other mechanical responses of BluePNTs to establish new benchmarks important to fundamental material characterization and practical device implementation.

We have performed simulations of both armchair and zigzag BluePNTs with various diameters and aspect ratios to study the size effect on the buckling characters of these BluePNTs. As a representative example, the results for an armchair (11,11) BluePNT with a length of $98.5 \text{ \AA}$ and a diameter of $19.7 \text{ \AA}$ are shown in Fig. 4. It is seen that when the BluePNT is subjected to axial compression, its strain energy steadily increases with rising strain, and the tubular structure is maintained until reaching a strain of 10.4% , where a sudden drop in the strain energy occurs; meanwhile, the cross-sectional circular structure collapses to release the excessive strain energy. This phenomenon is similar to those observed in CNTs.^{13,14} Our results show that both armchair and zigzag BluePNTs with small aspect ratios exhibit similar buckling behavior (see [supplementary material](#) for results on zigzag BluePNTs), indicating that although BluePNTs have more pronounced surface roughness, it can still be approximated as a shell-type structure that can be described by the continuum mechanics theory.

We next examine an armchair (11,11) BluePNT with an increased aspect ratio of $L/d = 15$ (diameter $19.7 \text{ \AA}$ and length $298.3 \text{ \AA}$), and find that the buckling mode changes to column type when the compressive strain reaches a critical value of 5.3% as shown in Fig. 5. For this BluePNT with a larger aspect ratio, the originally straight structure becomes deflected to release the excessive strain energy; however, the circular cross-sectional shape remains intact on this process. This observation is consistent with previously reported results on other nanotubes, such as those predicted by Zhang *et al.*¹⁸ for CNTs and those reported by Liu *et al.*³² for defective armchair BlackPNTs. Interestingly, according to Feliciano *et al.*,¹⁹ although the cross-sectional shape remains unchanged, further compression of the nanotube will lead to a larger bending curvature [see Fig. 5(c)], and when such curvature reaches another critical value, a secondary buckling behavior appears, i.e., a shell buckling. This phenomenon is also observed in our simulation for BluePNTs, as can be seen in Fig. 5, where another strain energy drop appears at the strain of 6.1% , where two

FIG. 3. Mechanical properties of BluePNTs under uniaxial strain. (a) Stress-strain relations for selected BluePNTs, with negative strain indicating BluePNTs under compression. (b)–(c) Extracted data from (a) showing the diameter dependent Young's modulus, fracture stress, and fracture strain, while blue triangles denote results for zigzag BluePNTs.

FIG. 4. Buckling of an armchair (11,11) BluePNT with a diameter of 19.7 Å and an aspect ratio of 5 under axial compression. The left panel shows the energy-strain relation where a sudden drop in the strain energy is seen at the strain of 10.4%, while the corresponding buckled structure is shown on the right.

kinks form as a distinct route to releasing the excessive built-up strain energy.

Our simulations for both armchair and zigzag BluePNTs exhibit the same trends as described above (see representative

FIG. 5. Buckling of an armchair (11,11) BluePNT with an aspect ratio of 15 under axial compression. The energy-strain curve is plotted in the top panel, while the representative tube structures near the critical strains marked in the strain energy plot are shown at the bottom.

results for zigzag BluePNTs in the [supplementary material](#)), indicating that although less strong, BluePNTs show deformation modes that are similar to those reported for nanotubes of carbon or boron nitride. At increasing aspect ratio, BluePNTs undergo a transition from the initial shell buckling mode to the column buckling mode; meanwhile, for BluePNTs with large aspect ratios, further compression results in a column-to-shell buckling mode transition. The general trends of critical buckling strains are shown in [Fig. 6](#), where it is seen clearly that with increasing aspect ratio, the initial critical buckling strain decreases and follows an analytic expression predicted by a previously proposed model¹⁸ $\epsilon_c = \pi^2 \frac{(d^2 + h^2)}{L^2}$, where d is the tube diameter, h is the tube wall thickness, and L is the tube length. It is also noted that for BluePNTs with small aspect ratios, the critical shell buckling strain increases with decreasing diameter.

Meanwhile, the secondary buckling strain shows a different trend as shown in [Fig. 6\(b\)](#), where for most of the BluePNTs, the critical shell buckling strain increases with their aspect ratios. This is because larger aspect ratios make BluePNTs harder to reach the critical bending curvature needed for shell buckling, in agreement with a previously proposed model¹⁹ for CNTs. Note that there are two exceptional points in [Fig. 6\(b\)](#) for the (8, 8) and (14, 0) BluePNTs with the aspect ratio of 15, whose critical shell buckling

FIG. 6. Critical buckling strain vs aspect ratio of BluePNTs. (a) Initial buckling strain, where the black dashed line is a plot to guide the eye and (b) secondary buckling strain for BluePNTs with large aspect ratios after the column buckling upon further compression.

strain decreases slightly. We attribute this phenomenon to numerical uncertainty, while the general trend remains consistent for most cases studied here and that reported for other nanotubes.^{18–20,32} Overall, the difference between the initial column buckling strain and the secondary shell buckling strain increases with the aspect ratio, as can be clearly observed in Fig. 6.

While our present results show that buckling modes of BluePNTs are very close to those previously seen in CNTs, another allotrope of black phosphorus offers an interesting case of contrasting behaviors. We show some representative results for BlackPNTs from our simulations in Fig. 7 to illustrate the difference. As

FIG. 7. Buckling behaviors of (a) an armchair (18,18) and (b) a zigzag (33,0) BlackPNT under uniaxial compression. Here, the diameter of the (18,18) BlackPNT is 25.8 Å and that of the (33,0) BlackPNT is 35.9 Å, and both BlackPNTs have the same aspect ratio of 5. When approaching the critical buckling strain, the cross-sectional shape of the armchair BlackPNT collapses to release the excessive strain energy, while the zigzag BlackPNT's wall swells instead, as illustrated by the representative snapshots shown in insets of (a) and (b). The critical initial buckling strain for selected BlackPNTs is shown in (c).

previously predicted by Kou *et al.*,⁹ black phosphorus is highly anisotropic in its mechanical properties due to its distinct puckering structural feature, especially when subjected to compression. As a result, when rolled into nanotubes, zigzag BlackPNTs and armchair BlackPNTs exhibit very different responses to axial compression. It is seen in Fig. 7(a) that when an armchair BlackPNT (a diameter of 25.8 Å and a length of 129.2 Å in this case) is under axial compression, the energy-strain curve is very similar to that of BluePNTs and a shell buckling mode is clearly observed. However, for all small aspect ratio zigzag BlackPNTs simulated in the present work, the tube wall swells locally when under compression to release the strain energy and the circular cross-sectional shape remains unchanged, as shown for the (33,0) BlackPNT (with a diameter of 35.9 Å and a length of 179.5 Å) in Fig. 7(b). Another notable difference is that for zigzag BlackPNTs with small aspect ratios, the initial buckling strain is larger than that of the armchair BlackPNTs with a similar size, indicating higher capability of adsorbing compressive strain energy, as is clearly seen in Fig. 7(c). This behavior is close to that of black phosphorus sheet under compression as predicted by Kou *et al.* using first-principles calculations,⁹ which is characteristic of the strong anisotropic nature of the properties of black phosphorus. With increasing aspect ratio, both armchair and zigzag BlackPNTs undergo a shell-to-column buckling transition and the critical strains are similar for both types of nanotubes, and we, therefore, do not discuss the mechanics in detail here. These results indicate that structures composed of blue phosphorus may have certain advantages compared to those based on black phosphorus in electromechanical devices because of the distinct contrasts in sensitivity to crystalline orientations.

IV. CONCLUSIONS

We have developed a Stillinger-Weber potential for molecular dynamics simulations of blue phosphorus by fitting to energetic and structural results from first-principles calculations. The resulting potential was adopted to examine the mechanical properties of BluePNTs under axial compression, evaluating the responses to changes in tube diameter, aspect ratio, and chirality. Our simulation results show that chirality has minimal influence on the buckling modes of BluePNTs; however, the diameter and aspect ratio play vital roles in their buckling behaviors. For BluePNTs with small aspect ratios, the critical buckling strain increases with decreasing diameter and only the shell buckling mode is observed. With increasing aspect ratio, the initial shell buckling transitions to column buckling. Meanwhile, the critical buckling strain decreases monotonically with the aspect ratio. Further compression to the already buckled BluePNTs leads to a column-to-shell buckling mode transition, and the critical buckling strain is also consistent with predictions from the continuum mechanics theory models. Comparison to BlackPNTs of similar sizes shows that BlackPNTs exhibit strong chirality dependent buckling modes, stemming from the highly anisotropic puckering structural characters of the black phosphorus sheet, which is distinct from those of blue phosphorus. Our present results are expected to stimulate further experimental and computational efforts to characterize nanotubes rolled from nonplanar 2D crystals similar to blue phosphorus and to investigate the underlying atomistic mechanisms for their structural and

mechanical properties. This line of work should provide valuable guidelines to rational designs of nanostructured systems for potential applications in functional electromechanical devices.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for a copy of the SW potential file for use in LAMMPS, descriptions of how to use the potential, and buckling behavior of zigzag (19, 0) BluePNTs with aspect ratios of 5 and 15 under compression.

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