Supplemental on-line material for:
High stability of faceted nanotubes and fullerenes of multi-phase layered phosphorus: A computational study

Jie Guan, Zhen Zhu, and David Tománek

NOMENCLATURE OF FACETED NANOTUBES

The nomenclature we introduce for faceted nanotubes is not as straight-forward as for non-faceted nanotubes. According to the main manuscript, the circumference of the polygonal cross section of an armchair nanotube is equal to $n_\alpha a_\alpha + n_{\beta_1} a_\beta + n_\gamma a_\gamma + n_{\beta_2} a_\beta$. In analogy, the circumference of the polygonal cross section of a zigzag nanotube would be equal to $n_{\gamma_1} a_\gamma + n_{\delta_1} a_\delta + n_{\gamma_2} a_\gamma + n_{\delta_2} a_\delta$. Connecting the strips with these widths will result in a unique nanotube and is not ambiguous. Ambiguity arises from assigning atoms along the connection line to either the phase on the one or on the other side of the connection line. As shown in Fig. S1, the same structure could be described by (n_α, n_β) and $(n_\alpha + 1, n_\beta - 1)$. This would lead to different values of n_α in the same a-PNT and different values of n_{γ_1} and n_{γ_2} in the same z-PNT. As we suggest in the main manuscript, we can avoid this ambiguity by selecting $n_\alpha = max$ in a-PNTs and $n_{\gamma_1} = max$ and $n_{\gamma_2} = max$ in z-PNTs.
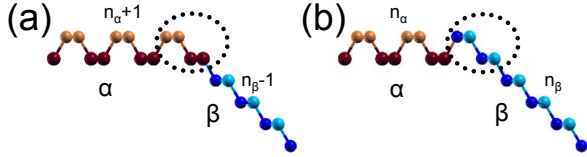

FIG. S1. (Color online) Source of ambiguity in the nomenclature of faceted nanotubes. In two identical junctions of phases α and β, atoms along the connection line, indicated by the dotted ellipse, may be assigned to the phase on either side.

STRUCTURAL VARIETY OF PHOSPHORENE NANOTUBES

As explained in the main manuscript, the shape of the phosphorene nanotube (PNT) a-PNT($n_\alpha,n_{\beta_1},n_\gamma,n_{\beta_2}$) with an armchair edge and of z-PNT($n_{\gamma_1},n_{\delta_1},n_{\gamma_2},n_{\delta_2}$) with a zigzag edge may vary significantly by changing the width n of the individual components. Only one example of an a-PNT with a C_3 symmetry and a z-PNT with a C_2 symmetry has been shown in Fig. 1 of the main manuscript. Additional examples of narrow armchair nanotubes are shown in Fig. S2(a) and of zigzag nanotubes in Fig. S2(b). Even though these nanotubes have a small average radius, they are unusually stable,
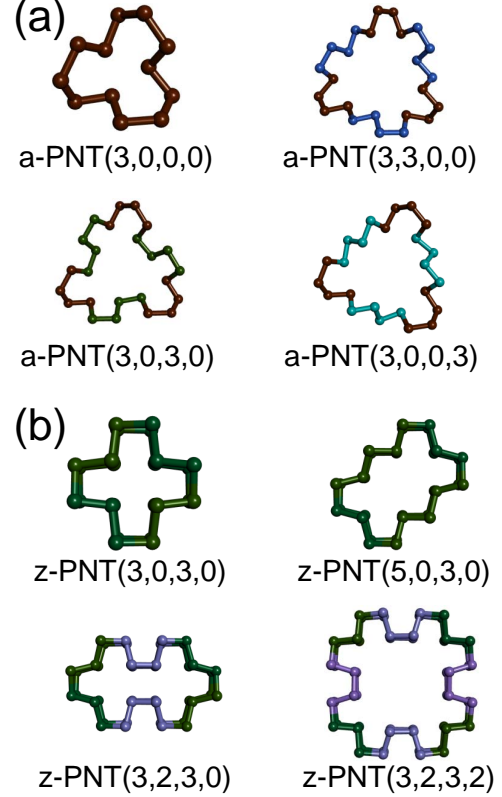

FIG. S2. (Color online) Cross-section geometry of selected (a) a-PNTs and (b) z-PNTs. Different structural phases are distinguished by color. The color coding is consistent with the main manuscript.

as seen in Fig. 3(a) of the main manuscript.

We also wish to point out that faceted nanotubes described here are not completely free of strain. Assuming that the optimum connection angles between narrow strips are the same as between semi-infinite planes provided in Reference [1], we do find that narrow strips of the different phases, connected at the optimum angle, would not form a perfect tube. Specifically, constituents of an armchair nanotube would ideally connect to 348° instead of 360°, requiring a small amount of additional bending to form a nanotube. Similarly, constituents of a zigzag nanotube would connect to 280° instead of 360°, requiring a larger amount of additional bending to form a nanotube. While this residual strain is very small, it is not negligible. As stated in the main manuscript, the stability of a particular nanotube is mainly determined by the different stabilities of the constituent phases and,

to a much smaller degree, by this residual strain.

ELECTRONIC BAND STRUCTURE AND FRONTIER ORBITALS IN PHOSPHORENE NANOTUBES

As seen in Fig. 3(c) of the main manuscript, zigzag PNTs have typically small, but nonzero band gaps. Only the narrowest z-PNT(3,0,3,0) is metallic, with two bands crossing the Fermi level, as seen from its band structure in Fig. S3(a). Wider z-PNTs are all narrow-gap semiconductors, as seen in the representative band structure of the z-PNT(5,0,5,0) shown in Fig. S3(b). To find the reason for the anomalous electronic structure of the z-PNT(3,0,3,0), we examined the charge distribution in the frontier orbitals and display it in Fig. S3(c). For the sake of comparison, we display the analogous charge distribution in the wider z-PNT(5,0,5,0) in Fig. S3(d). We used a somewhat arbitrary definition of frontier orbitals by the energy range $E_F - 0.1$ eV$< E < E_F + 0.1$ eV in the metallic nanotube in Figs. S3(a) and S3(c). Since no states are found in this energy range in the semiconducting z-PNT(5,0,5,0), we expanded the energy range associated

with frontier orbitals to $E_F - 0.2$ eV$< E < E_F + 0.2$ eV in Figs. S3(b) and S3(d). We find the frontier orbitals to display a dominant p character with a small s admixture, causing them to point radially in or out. Whereas there is no overlap between such orbitals on neighboring sites in the wider z-PNT(5,0,5,0) in Fig. S3(d), we observe a significant overlap between sites along the inner perimeter, which are third neighbors to each other and come closer in the narrow z-PNT(3,0,3,0), shown in Fig. S3(c). The origin of conduction in the narrow z-PNT(3,0,3,0) are the conduction channels formed by these rehybridized states. One beneficial effect of the rehybridization across the diameter is an improved rigidity of the nanotubes.
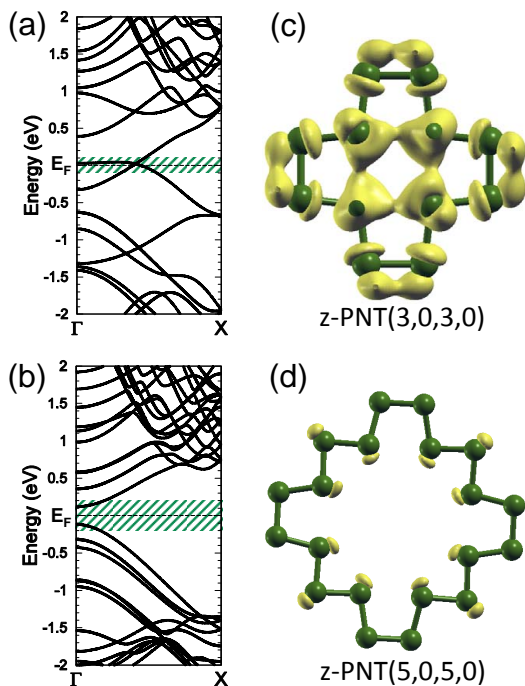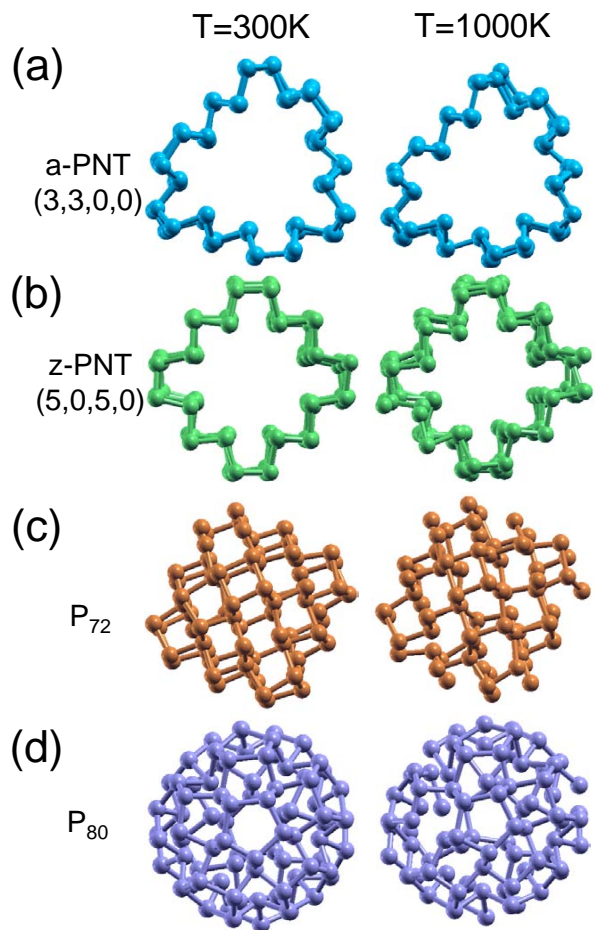

FIG. S3. (Color online) Electronic band structure of (a) the z-PNT(3,0,3,0) and (b) the z-PNT(5,0,5,0) nanotube. The region associated with frontier orbitals is highlighted by the green shading in the energy range $E_F - 0.1$ eV$< E < E_F + 0.1$ eV in (a) and $E_F - 0.2$ eV$< E < E_F + 0.2$ eV in (b). Electron density ρ_f associated with frontier states in (c) the z-PNT(3,0,3,0) and (d) the z-PNT(5,0,5,0) nanotube, superposed with ball-and-stick models of the structures. ρ_f is represented by the isosurface value 8×10^{-4} e/Å^3.

FIG. S4. (Color online) Snap shots of canonical molecular dynamics simulations at $T = 300$ K and $T = 1000$ K depicting structural changes in phosphorus nanotubes and fullerenes. Nanotubes are represented by (a) the armchair a-PNT(3,3,0,0) and (b) the zigzag z-PNT(5,0,5,0). Fullerenes are represented by (c) P_{72} and (d) P_{80}. The nanotubes are shown in end-on view.

STABILITY OF FACETED NANOTUBES AND FULLERENES AT HIGH TEMPERATURES

Structural stability at $T = 0$ says little about stability at high temperatures, where thermally activated structural changes may take place. A direct way to probe the stability of faceted phosphorus nanotubes and fullerenes at high temperatures is by performing molecular dynamics (MD) simulations. Results of our canonical MD simulations are presented in Fig. S4 as structural snap shots of the a-PNT(3,3,0,0) and the z-PNT(5,0,5,0) nanotube and the P_{72} as well as the P_{80} fullerene at $T = 300$ K and $T = 1,000$ K. To avoid artifacts associated with constraints imposed on nanotubes by finite-size unit cells, we used supercells containing 3 primitive unit cells. We used 1 fs time steps to cover between 0.8-3 ps, depending on system and temperature. We found structural changes to be minimal at room temperature. We observed larger atomic motion at $T = 1,000$ K, which lies slightly above $T_M = 863$ K, the melting point of red phosphorus [2], but no indication of concerted structural changes to a different allotrope. We thus conclude that faceted nanotubes and fullerenes display a similar thermal stability as monolayers of α-, β-, γ- and δ-phosphorene discussed previously [1, 3]. Since the cohesive energies of faceted nanotubes and fullerenes are at most 0.2 eV/atom lower than bulk black phosphorus, we expect these nanostructures to coexist with the bulk structure under experimental conditions.

The following movies, which illustrate the dynamics at high temperatures better than structural snap shots, are part of the Supplemental Material:

- `a-PNT3300-300K.avi` represents the a-PNT(3,3,0,0) at $T = 300$ K in end-on view;
- `a-PNT3300-1000K.avi` represents the a-PNT(3,3,0,0) at $T = 1000$ K in end-on view;
- `z-PNT5050-300K.avi` represents the z-PNT(5,0,5,0) at $T = 300$ K in end-on view;
- `z-PNT5050-1000K.avi` represents the z-PNT(5,0,5,0) at $T = 1000$ K in end-on view;
- `P72-300K.avi` represents the fullerene P_{72} at $T = 300$ K;
- `P72-1000K.avi` represents the fullerene P_{72} at $T = 1000$ K;
- `P80-300K.avi` represents the fullerene P_{80} at $T = 300$ K;
- `P80-1000K.avi` represents the fullerene P_{80} at $T = 1000$ K.

The total run time of all movies has been reduced to 0.8 ps for easy comparison.

EFFECT OF VAN DER WAALS INTER-WALL INTERACTIONS IN MULTI-WALL STRUCTURES

Since both multi-wall nanotubes and fullerenes are related to multi-layer phosphorene, we expect van der Waals inter-wall interactions to play a similar role in these systems. We studied this effect by comparing the equilibrium structure and stability of the z-PNT(5,0,5,0)@(9,0,9,0) double-wall nanotube, shown in Fig. 4(a) of the main manuscript, by artificially switching on or off the effect of van der Waals interactions as described by the optB86b-vdW functional [4, 5]. Due to the constrained nature of the tubular system, we found that the van der Waals interactions do not modify the geometry. Similar to a phosphorene double-layer, presence of van der Waals interactions stabilizes the double-wall system by $\lesssim 0.1$ eV/atom. As anticipated, the stability and the structure of single-wall a-PNT(3,3,0,0) and z-PNT(5,0,5,0) nanotubes were not affected by the presence or absence of the van der Waals interaction in the optB86b-vdW implementation.

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