Nanoscale

PAPER

Cite this: Nanoscale, 2016, 8, 14778

Acute mechano-electronic responses in twisted phosphorene nanoribbons†

Woosun Jang, Kisung Kang and Aloysius Soon*

Many different forms of mechanical and structural deformations have been employed to alter the electronic structure of various modern two-dimensional (2D) nanomaterials. Given the recent interest in the new class of 2D nanomaterials – phosphorene, here we investigate how the rotational strain-dependent electronic properties of low-dimensional phosphorene may be exploited for technological gain. Here, using first-principles density-functional theory, we investigate the mechanical stability of twisted one-dimensional phosphorene nanoribbons (TPNR) by measuring their critical twist angle (θc) and shear modulus as a function of the applied mechanical torque. We find a strong anisotropic, chirality-dependent mechano-electronic response in the hydrogen-passivated TPNRs upon vortical deformation, resulting in a striking difference in the change in the carrier effective mass as a function of torque angle (and thus, the corresponding change in carrier mobility) between the zigzag and armchair directions in these TPNRs. The accompanied tunable band-gap energies for the hydrogen-passivated zigzag TPNRs may then be exploited for various key opto-electronic nanodevices.

Introduction

Materials with low-dimensionality are known to exhibit many interesting basic properties that can be vastly different from their bulk counterparts. Recently, there has been a huge interest in various two-dimensional (2D) nanomaterials after the successful isolation of graphene, and single- and few-layered transition metal dichalcogenides (TMDCs).

However, semi-metallic behavior of single-layered graphene and deep defect states observed in 2D TMDCs have hindered usage in modern nanodevices which could greatly benefit from the many outstanding properties that these low-dimensional nanomaterials have, e.g. high carrier mobility, low effective mass, and excellent on/off ratios. This has motivated many to push the boundaries and limits of these novel layered nanomaterials by chemically and physically altering their equilibrium structures.

Global R Institute and Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea. E-mail: aloysius.soon@yonsei.ac.kr†

Electronic supplementary information (ESI) available: Figures: atomic structure of pristine single-layered phosphorene showing the armchair and zigzag directions. DFT-PBE electronic band structures of H-TPNRs as a function of θ. Comparison of the electronic band structure and its derived carrier effective masses, \(m^*\), of twisted H-TPNRs with (left) PBE and (right) HSE06 xc functionals. Population of P-to-P distances in H-TPNRs. Band energies at VBM and CBM in TPNRs with respect to the lattice dilation. Tables: computed carrier effective masses and mobilities in H-TPNRs. Parameters and constants used for calculations are listed accordingly. See DOI: 10.1039/c6nr04354b

† For instance, dimensionality-, strain-, and dopant-engineering are just some of the various attempts to modulate and tailor the desired electronic band-gap energy of these nanomaterials. Although many guiding principles have been put forth, it is still very challenging to design and engineer new 2D nanomaterials to cover a wide enough range of the energy spectrum for niche opto-electronic applications. Graphene and its derivatives still possess too small a band-gap while the TMDC family retains its intrinsic large band-gap energies, which leaves the mid-energy spectrum largely untapped. There is a pressing need to find new methods and new materials to “stand in the gap”.

Of late, the discovery of a new class of 2D layered nanomaterial – phosphorene, which is the 2D counterpart of bulk black phosphorus – has brought new excitement to this community by demonstrating the possibility of filling this mid-energy spectrum gap. Despite the fact that pristine single-layered phosphorene has a band-gap energy of 1.45 eV, it has been proposed that careful engineering of this 2D element (e.g. by applying mechanical strain, nanostructuring, or chemical doping) could easily tune the band-gap energy of phosphorene from ∼0 to close to 2 eV, without degrading its impressive intrinsic properties such as mechanical flexibility and high carrier mobility. This has definitely opened up new doors to bridge the much desired mid-energy spectrum gap e.g. in novel display technologies.
ribbons (GNRs) that applying both lateral and shear strain had a profound influence on their opto-electronic properties.\textsuperscript{16,19–23} It is thus intriguing to ask how one might exploit a tunable electronic band-gap energy from mechanically deformed phosphorene nanoribbons, given their higher mechanical flexibility.\textsuperscript{24}

In this study, using first-principles density-functional theory (DFT) calculations, we begin by systematically examining the thermodynamic and mechanical stability of pristine and hydrogen-passivated twisted phosphorene nanoribbons (TPNRs) with two different edge-chiralities. Due to the puckered structure of phosphorene as shown in Fig. 1a, this naturally results in the so-called pristine armchair (P-APNR) and zigzag (P-ZPNR) configurations (see Fig. S1†). Given that the dangling bonds at the edge of the TPNRs may affect their overall electronic structure, we have also considered hydrogen-passivated TPNRs (i.e. H-APNR and H-ZPNR denoting the H-passivated armchair and zigzag TPNRs, respectively).

To apply the out-of-plane “twist” (or vortical deformation) to these phosphorene nanoribbons within the periodic simulation model, one will have to carefully consider its periodicity, twisting angle, and twisting axis (Fig. 1b). In this work, we have chosen a 6-atom (∼8.5 Å) wide APNR and 12-atom (∼13.3 Å) wide ZPNR as representative models to study the effects of mechanical twisting on their electronic structures. Unlike their atomically-flat “2D cousins” – graphene and hexagonal BN, it is non-trivial to model periodically TPNRs due to their in-plane buckled geometry. Here, we define the twisting angle (θ) as the measured angle between two adjacent planes, as shown in Fig. 1c, where each plane consists of six P atoms in the same atomic-plane perpendicular to the twisting axis (which is along the c-direction of the simulation supercell; see Fig. 1b). Accordingly, θ is then calculated using

\[ \theta = \frac{180^\circ l}{2L}, \]

where L and l denote the length (in the c-direction) of our twisted supercell and non-twisted unit cell, respectively. The l of APNR is calculated to be 4.39 Å, and that of ZPNR is 3.32 Å.

To achieve the desired θ, we have varied the length of our simulation supercell (L) in the c-direction while ensuring that the periodically repeated images are 180° twisted from its neighboring image (as depicted in Fig. 1b) to preserve the desired θ. To keep our calculations computationally feasible, θ for APNR ranges from 0 to 36° while that for ZPNR spans from 0 to 11.25°. This results in a fairly large periodic supercell model of up to almost 200 atoms per supercell for the ZPNRs and up to about 150 atoms per supercell for the APNRS.

**Results and discussion**

To systematically investigate the thermodynamic stability of these TPNRs, we define and calculate the enthalpy of formation, Δ\(H^f\) (per atom) using the following equation:

\[ \Delta H^f = \frac{E_{\text{tot}} - \left(N_P E_{\text{Pbulk}} + N_H E_{\text{Hmlc}}\right)}{N_P + N_H}, \]

where \(E_{\text{tot}}, E_{\text{Pbulk}}, E_{\text{Hmlc}}\), \(N_P\) and \(N_H\) are the total energies of the TPNR, bulk black phosphorus, hydrogen molecule, the total number of P atoms and H atoms in the TPNR, respectively. \(\Delta H^f\) as a function of the length-normalized θ is plotted in Fig. 2.

As shown in Fig. 2, due to the large number of dangling bonds in the pristine TPNRs (i.e. P-APNRs and P-ZPNRs), \(\Delta H^f\) is calculated to be positive (i.e. endothermic) for these TPNRs.\textsuperscript{25,26} Interestingly, the order of preference for P-APNR to P-ZPNR changes with increasing θ, and this corroborates well

![Fig. 1. Atomic structures of (a) single-layered phosphorene and (b) the twisted phosphorene nanoribbon. The twisting angle (θ) is defined in (c) where the twisting vortical axis is presented in a green straight arrow in (b) and a green dot in (c). P atoms in the same plane perpendicular to the twisting axis are depicted in the same color (red and blue) to aid viewing.](image)

![Fig. 2. Calculated formation enthalpy (\(\Delta H^f\)) of P-APNR (empty orange), H-APNR (filled orange), P-ZPNR (empty blue) and H-ZPNR (filled blue) as a function of θ per unit length. Solid lines between each point are to guide the eyes.](image)
with other reports\textsuperscript{18,24} where P-APNR was predicted to be mechanically more flexible than P-ZPNR, hence requiring less energy to twist in the armchair direction.

Upon H-passivation, we find that the removal of the edge dangling bonds lowers the $\Delta H^f$ of the TPNRs, with H-APNRs slightly more thermodynamically stable than H-ZPNRs. For all considered $\theta$, the $\Delta H^f$ of H-APNRs and H-ZPNRs is exothermic and this could imply that H-passivated TPNRs may well form under experimental growth conditions where hydrogen or hydrogen-containing growth precursors are present.\textsuperscript{27}

In addition, it was recently reported that many polymorphs of phosphorene are almost energetically degenerate (i.e. having relative energy differences within a couple of meV per atom), and in this work, it may well be plausible for these TPNRs to undergo (local) phase transformation given the appreciable change in the $\Delta H^f$ under vortical strain.

To investigate the possibility of a pressure-induced phase transformation in the TPNRs studied in this work, we have carefully examined the local atomic arrangements in the nanoribbons and compared to those of all reported polymorphs: namely the $\beta$, $\gamma$, and $\delta$-phase as reported in ref. 28 and 29, as well as the most recently discovered $\epsilon$, $\zeta$, $\eta$, and $\theta$-phases in ref. 30. In the former group of structures, they have a distinctive arrangement of tetrahedrally coordinated P atoms in a 2D lattice, and $P_2$ square or $P_2$ pentagon units in the latter newer group. These characteristic geometric features are not found in the TPNRs studied in this work. We argue that these (local) phase transitions might well be kinetically hindered when a vortical strain is applied to these nanoribbons.

Now, turning to the mechanical behavior of these TPNRs, we will assess their mechanical stability by calculating the critical twisting angle ($\theta_c$) for all TPNRs, which are the $\theta$ for APNRs and ZPNRs, respectively, can be calculated using the following equations:

$$\theta_c^{(z)} = \frac{L}{d} \cos^{-1} \left(1 - \frac{4(\varepsilon_m + \varepsilon_m^2/2)}{(w/d - \sqrt{3})^2}\right),$$

$$\theta_c^{(z)} = \frac{2L}{\sqrt{3}d} \cos^{-1} \left(1 - \frac{4(\varepsilon_m + \varepsilon_m^2/2)}{w/d(w/d - 1)}\right),$$

where $d$ and $w$ denote the longest P-P bond distance in a cell and the width of the TPNR upon relaxation. Here, $\varepsilon_m$ is defined as $\frac{d - d^{rel}}{d^{ref}}$ where $d^{rel}$ for APNR and ZPNR is deducted as 2.43 Å (at 32% of maximum lateral strain) and 2.46 Å (at 28% of maximum lateral strain), respectively from ref. 24.

These critical twisting angles $\theta_c$ for all TPNRs are plotted in Fig. 3 as a function of $L$. Based on this simple model, we find that both P-APNRs and H-APNRs can afford higher twisting angles before mechanically destabilizing, as reflected by the steeper gradient in Fig. 3. Again, this corroborates well with previous reports\textsuperscript{18,24} where APNRs are indeed found to be more flexible. More interestingly, H-passivation is found to not only thermodynamically stabilize these TPNRs, but it actually preserves their good mechanical stability without deteriorating their mechanical flexibility. In all cases, we find an almost perfect linear relationship between $\theta_c$ and $L$, which is very similar to the case of twisted graphene nanoribbons of varying widths.\textsuperscript{21}

Furthermore, recent studies\textsuperscript{31,32} on the lattice dynamics of strained 2D phosphorene sheets (i.e. for ±10% of lateral strain and ~16% of shear strain along both armchair and zigzag directions) reported a noticeable negative frequency mode in the phonon dispersion curve when the compression strain of more than 3% (or a shear strain more than 11%) was applied. Interestingly, a tensile strain of up to 10% did not result in any lattice dynamic instability, urging us to countercheck the mechanical stability of the TPNRs studied in this work.

To estimate the effect of bond stretching and compression in the TPNRs studied in this work, we have evaluated the P-to-P distance population via the radial distribution function, as shown in Fig. S6.\textsuperscript{1} From this analysis, we conclude that the P-P bonds in the TPNRs are compressed not more that 1.8% (which is also less than the 3% reported in ref. 31 and 32) and are stretched by ~8.5% (which is also less than the limit of 10% reported). Thus, we argue that our TPNRs are considered to be mechanically stable within this first estimate.

Besides evaluating the mechanical stability of TPNRs, one might also be interested to study how twisting of these phosphorene nanoribbons might affect their mechanical properties such as the shear modulus ($G$), and how much those $G$ values are different compared to other low-dimensional nanostructures. To estimate $G$ from our DFT calculated total energies, we define the angular/vortical strain, $\tau$ as\textsuperscript{33}

$$\tau = \frac{1}{V_0} \frac{dE}{d\theta},$$

where $V_0$ and $E$ are the volume of the non-twisted unit cell and the volume-normalized formation energy of the TPNR at the corresponding $\theta$, respectively. We perform a 2nd-order poly-
systems. reported values of in this work are listed in Table 1, and compared to the smooth and continuous curve, as shown in Fig. 4. This journal is © The Royal Society of Chemistry 2016

Next, we determine $G$ by simply taking the 2$^{nd}$ derivative, as given by

$$G = \frac{1}{V_0} \frac{\partial^2 E}{\partial \theta^2}.$$  

The estimated values of $G$ for the various TPNRs considered in this work are listed in Table 1, and compared to the reported values of $G$ for other low-dimensional nanomaterial systems.\textsuperscript{20,24,34–36}

Referring to Table 1, we see that the APNRs have a much smaller $G$ than the ZPNRs. This follows the consistent trend that APNRs are more flexible than the ZPNRs (as also found from our analysis of the $\theta_c$ as well as their variation in $\Delta H^f$ above). Although H-passivation increases the $G$ values for the TPNRs, they are still comparable to other reports on bulk phosphorus (~20 to 40 GPa).\textsuperscript{24,34} In contrast, graphene and graphene nanoribbons show very high values of $G$, proving that these carbon-based low-dimensional nanostructures are far more mechanically rigid than their phosphorus-based counterparts.

Next, we will focus and discuss the electronic structure of the thermodynamically stable H-passivated TPNRs. The variation in the DFT-HSE06\textsuperscript{37,38} band-gap energy, $E_g$ of H-APNRs and H-ZPNRs, as a function of the normalized twisting angle is shown in Fig. 5. For the most stable H-APNRs, we find a rather nominal variation in $E_g$ when $\theta$ is changed. The $E_g$ remains fairly constant at about 1.9 eV and gradually increases to 2.1 eV at higher twisting angles. From our calculations, we conclude that H-APNRs, though energetically the most stable, offer only a very narrow tunability of the $E_g$ with vortical twisting.

In contrast, H-ZPNRs are found to display a much wider range of $E_g$ changes. In the untwisted case, they exhibit a fairly large $E_g$ of 2.5 eV which decreases sharply (but rather linearly) to 0.95 eV at higher twisting angles, proving their usefulness in covering a wider range of the energy spectrum for opto-electronic applications such as photovoltaics and displays (see Fig. 5).

Having seen how the band gap energies for H-ZPNRs change acute as a function of vortical deformation, we proceed to calculate and estimate the effective masses and mobilities of the electron ($m_{\text{ee}}, \mu_e$) and the hole ($m_{\text{hh}}, \mu_h$) for both the H-APNRs and H-ZPNRs.

In this work, the $m^*$ of both the electron and the hole is calculated by using the equation $h^2 \left( \frac{\delta^2 E(k)}{\delta k^2} \right)^{-1}$, where $h$ is the reduced Planck constant. We determine the inverse of the second derivative of the energy–$k$-space relation, $E(k)$ from the

![Fig. 4](image-url) Normalized formation energy (per unit volume) of P-APNR (empty orange), H-APNR (filled orange), P-ZPNR (empty blue) and H-ZPNR (filled blue) as a function of $\theta$. Solid lines: parabolic regression relations.

![Fig. 5](image-url) (Left) $E_g$ variation of H-APNR (orange) and H-ZPNR (blue) as a function of $\theta$ per unit length. Solid lines are to aid viewing. (Right) $E_g$ variation of various low-dimensional nanomaterials in comparison with the solar irradiation spectrum and potential opto-electronic applications (as adapted from ref. 11).
DFT-PBE electronic band structure calculation, using 5 energy values within a parabolic band approximation. We have cross-checked that the band curvatures at both band edges are fairly similar in both PBE and HSE06 calculations, resulting in almost identical values of $m^*$ calculated with the two xc functionals (see ESI, Fig. S4 and S5†). Moreover, the calculated $m_h^*$ and $m_e^*$ with zero strain show reasonably good agreement with previously reported values39,40 (see ESI, Tables S1 and S2†).

In the calculation of the carrier masses, $m^*$ with the approximations stated above, we observe that the values obtained (especially so for the hole carriers) are quite sensitive and may vary greatly. For instance, the calculated value for the $m_h^*$ in the zigzag direction (where the carrier effective masses in the PNRs are argued to be comparable to those obtained from the analogous directions in 2D phosphorene)39,40 has been reported to range from 1.20 to 13.09$m_0$.25,39,41,42

Other effects that might influence the reliability of these effective mass calculations have also been suggested, such as the inclusion of spin–orbit coupling effects and band folding at the zone boundaries. Qiao et al. previously reported that the phosphorus atom is not sufficiently heavy to induce a noticeable change in the band dispersion.42 Following this argument, the spin–orbit coupling effects are neglected in this work.

As shown in Fig. S2 and S3 in the ESI,† the calculated electronic band structure of these H-TPNRs exhibits very flat bands near the valence band edges, and they may strongly influence our calculated $m_h^*$ within the parabolic band approximation. Therefore, the absolute values of carrier effective masses calculated in this work must be considered with caution. However, we believe that the responses (i.e. changes) of the effective masses and the carrier mobilities to the applied vortical twist on these H-TPNRs may be thought to be meaningful.

To compare with other reported in-plane strain effects, in this work, we compute the responses of the effective masses and carrier mobilities of the electron as well as the hole with respect to the untwisted case as a function of the twisting angle. The calculated changes to the effective masses, $\Delta m_e^*$ and $\Delta m_h^*$ for H-APNRs and H-ZPNRs are then plotted with respect to $\theta$ per unit length in Fig. 6a and b, where $m_e^*$ (and $m_h^*$) for the untwisted H-APNR and H-ZPNR are calculated to be 0.22 (and 0.19) and 1.23 (and 4.03)$m_0$, respectively. This is, overall, in line with earlier reports where the $m^*$ of both carriers in the phosphorene nanoribbon is known to be much lighter in the armchair direction than that in the zigzag direction.39,40

In Fig. 6a, a very nominal linear increase in the change of the electron effective mass of H-APNRs is observed upon twisting (i.e. $\Delta m_e^* > 0$). In a like manner, it has been previously reported that an external lateral strain (of $\sim$ 4 to 6%) applied to 2D phosphorene greatly inhibits the electron mobility along the armchair direction.34 From our calculations, we find this gradual increase in $m_e^*$ upon twisting has indeed an adverse effect on the electron mobility for the H-APNRs (see the discussion below).

On the other hand, a rather interesting trend is found for H-ZPNRs where $\Delta m_e^*$ is found to be always less than zero. For the H-ZPNRs, a small twist angle sharply decreases $m_e^*$ by almost $-1.0m_0$ where after which, upon further twisting, rises close to the value of the untwisted nanoribbon, albeit still less than the original value of $1.23m_0$. In comparison with the H-APNRs, this acute response of the H-ZPNRs to the vortical deformation is found to be almost an order of magnitude larger than that of H-APNRs.

For $\Delta m_h^*$ of H-APNRs and H-ZPNRs, we find a monotonic increase of $m_h^*$ for the H-APNRs and no observable trend for that of H-ZPNRs, as shown in Fig. 6b. Here, as cautioned above, we do interpret with care as we find that due to band zone folding in our supercell structures, the valence band edges (especially) are almost flat about the $\Gamma$-point (as clearly shown in Fig. S2 and S3 in the ESI†). Nevertheless, as expounded in ref. 43, we do indeed see a difference in the responses of both the $m_e^*$ and $m_h^*$ upon applying a vortical strain in these H-TPNRs, very much similar to the case where changes to the electron mobility are the most sensitive under external mechanical distortions.43
To relate our calculated $m^*$ values to their carrier mobility $\mu$, we further calculate and approximate $\mu$ along the nanoribbon direction by adopting the following equation: $^{40,41,44-46}$

$$\mu = \frac{e\hbar^2}{k_B T (m^*)^{3/2} E_1^2}. \quad (7)$$

Here, $e$, $\hbar$, $k_B$, and $T$ denote the elementary charge, reduced plank constant, Boltzmann constant, and temperature (where $T = 300$ K), respectively. $C$ is the elastic constant obtained by $\rho \nu \lambda$, where $\rho$ and $\nu$ are designated as the atomic mass density and sound velocity along the longitudinal direction of the nanoribbon. We have adopted the longitudinal sound velocity values of pristine phosphorene under shear strain from ref. 32. The deformation potential constant $E_1$ is extracted from the fitted slope of the CBM and VBM band energies of the untwisted H-TPNR supercell (with respect to the vacuum energy) as a function of in-plane lattice strain. The derived parameters and constants used for the calculations can be found in Tables S1 and S2 of the ESL.$^1$

In a similar fashion, we define the change in (i.e. the responses of) carrier mobilities, $\Delta \mu_e$ and $\Delta \mu_h$ with respect to $\mu$ of the untwisted nanoribbons, and plot their variation as a function of $\theta$ per unit length in Fig. 6c and d. For the untwisted H-APNR and H-ZPNR (Fig. 6c), $\mu_e$ is found to be $10.35 \times 10^4$ and $0.14 \times 10^3$ cm$^2$V$^{-1}$s$^{-1}$, respectively, while $\mu_h$ is found to be $2.26 \times 10^4$ and $0.44 \times 10^3$ cm$^2$V$^{-1}$s$^{-1}$, respectively. Here, a similar acute response in $\mu_e$ is also found for H-ZPNR while a relatively gentle change is seen for H-APNR. In accord with the observed response of $\Delta \mu_e$ in H-ZPNR (in Fig. 6a), a small vortical deformation angle scales up its $\mu_e$ rapidly by almost $5.13 \times 10^4$ cm$^2$V$^{-1}$s$^{-1}$, and drops quickly to the original value of the untwisted case upon further twisting. For H-APNR, a monotonic drastic decrease of $\Delta \mu_e$ is found as the vortical deformation angle increases, aligning nicely with the reported detrimental effect of external strain in the armchair direction for 2D phosphorene.$^{43}$

In Fig. 6d, the $\Delta \mu_e$ of both H-APNRs and H-ZPNRs is found to vary minimally with increasing twisting angle. Here, we rationalize these interesting mechano-electronic responses of $\mu_e$ by analyzing the HSE06 calculated partial electron densities at the CBM for both H-APNRs and H-ZPNRs. To illustrate our point, we have plotted the CBM partial electron densities for H-APNR at $\theta = 6.36 \times 10^{-3}$ rad Å$^{-1}$ and H-ZPNR at $\theta = 3.29 \times 10^{-3}$ rad Å$^{-1}$ as an example in Fig. 6e and f, respectively. This qualitative picture may help in our understanding of the electron’s “transport channel” through the nanoribbon and how this channel could be inhibited by mechanical torque distortions.

We can clearly observe that most of the CBM states for H-APNR are located in the middle of the nanoribbon (Fig. 6e) where vortical deformation to the structure will have a minimal impact on these states as opposed to those of H-ZPNR which are largely localized along the edges of the nanoribbon (Fig. 6f). We can thus infer that angular/rotational distortions to the H-ZPNRs will then impose a more acute mechano-electronic response than that for H-APNRs. This corroborates well with the fact that we see larger P–P and P–H bond lengthening at the edges as opposed to the P–P bonds near to the center axis of the nanoribbon.

Conclusions

In conclusion, using first-principles DFT calculations, we have carefully examined the mechano-electronic responses for various pristine and H-passivated phosphorene nanoribbons with two different edge chiralities (i.e. the armchair and zigzag configurations). We have found that H-passivation energetically stabilizes the TPNRs over the pristine structures, with H-APNRs being the most stable. By calculating their critical twisting angles and estimating their shear moduli, we find that TPNRs (especially the APNRs) are significantly more flexible compared to other carbon-based 2D nanomaterials like graphene and graphene nanoribbons. This increased mechanical flexibility can be exploited to tune the band-gap energies of these TPNRs, in particular for H-ZPNRs, where a fairly wide range of the energy spectrum can be made available by simply applying mechanical twisting to these very stable H-passivated ZPNRs. In addition, by calculating the changes to the carrier effective masses and mobilities for H-TPNRs, we report a marked difference in these changes as a function of the vortical angle between the zigzag and armchair directions in these TPNRs. We envisage that these twisted 1D nanoribbons of phosphorus can be great contenders to potential new optoelectronic applications in e.g. photovoltaics and displays.

Methods

All calculations are based on periodic density-functional theory (DFT) using the projector-augmented wave (PAW) method, as implemented in the Vienna Ab initio Simulation Package (VASP)$^{47,48}$ with a planewave kinetic energy cutoff of 500 eV. The generalized gradient approximation (GGA) due to Perdew, Burke and Ernzerhof (PBE)$^{49}$ exchange–correlation functional is used for all geometric relaxation and total energy calculations. For the Brillouin-zone integrations, a Γ-centered $k$-point mesh equivalent to the reciprocal distance of 0.2 Å$^{-1}$ is employed for all geometry optimizations while a smaller spacing of 0.15 Å$^{-1}$ is used for the electronic structure calculations. To minimize unphysical interactions between periodically repeating images, a vacuum region of at least 10 Å is enforced in both $x$- and $y$-directions, where the nanoribbon is aligned parallel to the $z$-axis. To afford a more accurate description of the electronic structure of these TPNRs, we employ the HSE06 hybrid functional.$^{37,38}$ All calculations have been carefully tested systematically for convergence with respect to kinetic energy cutoff, $k$-point grid, and the vacuum separation between repeated images, where total energies and forces do not vary more than 20 meV and 0.02 eV Å$^{-1}$, respectively.
Acknowledgements

We acknowledge that this work is supported from the Basic Science Research Program by the NRF [National Research Foundation of Korea, Grant No. 2014R1A1A1003415]. Computational resources have been provided by the KISTI (Korea Institute of Science and Technology Information) supercomputing center [KSC-2015-C3-030].

References

32. B. Sa, Y.-L. Li, Z. Sun, J. Qi, C. Wen and B. Wu, Nanotechnology, 2015, 26, 215205.
Supporting Information:

Acute Mechano-Electronic Responses in Twisted Phosphorene Nanoribbons

Woosun Jang, Kisung Kang, and Aloysius Soon*

Global E3 Institute and Department of Materials Science and Engineering,
Yonsei University, Seoul 120-749, Korea

(Dated: June 23, 2016)

FIG. S1. (Color online) Top- and side-views of the atomic structure of pristine single-layered phosphorene in (a) and (b), respectively. Atoms with different vertical height are distinguished by the color of atoms. Armchair and zigzag direction is shown in red and blue arrow accordingly.

* Corresponding author. E-mail: aloysius.soon@yonsei.ac.kr
FIG. S2. (Color online) DFT-PBE electronic band structure of H-APNRs as a function of $\theta$.

FIG. S3. (Color online) DFT-PBE electronic band structure of H-ZPNRs as a function of $\theta$.

FIG. S4. (Color online) Comparison of the electronic band structure and its derived electron effective mass, $m_e^*$ of untwisted H-APNR with (left) PBE and (right) HSE06 xc functional.
**FIG. S5.** (Color online) Comparison of the electronic band structure and its derived electron effective mass, $m^*_e$ of untwisted H-ZPNR with (left) PBE and (right) HSE06 $xc$ functional.

**FIG. S6.** (Color online) Population of P-to-P distances in H-APNRs and H-ZPNRs. ±10% range is shown in grey shaded area. Optimized in-plane and out-of-plane P-P bond in unstrained phosphorene is shown in blue dotted lines.
FIG. S7. (Color online) Band energy of CBM and VBM in H-APNR (left) and H-ZPNR (right) with respect to the lattice dilation. HSE06 functional is used to calculate band energies. Fitting parameters (a and b) and standard deviations (σa and σb) are listed in the table.

TABLE S1. Computed effective masses and mobilities in H-APNRs. Parameters and constants used for the calculations are listed accordingly.
TABLE S2. Computed effective masses and mobilities in H-ZPNRs. Parameters and constants used for the calculations are listed accordingly.

<table>
<thead>
<tr>
<th>$\theta$ (degree)</th>
<th>$\theta/L$ ($10^{-3}$ rad/$\text{Å}$)</th>
<th>$v_0$ (km s$^{-1}$)</th>
<th>$C$ (J m$^{-2}$)</th>
<th>$E_{1}^{\text{CBM}}$ (eV)</th>
<th>$E_{1}^{\text{VBM}}$ (eV)</th>
<th>$m_e^*$ ($m_0$)</th>
<th>$m_h^*$ ($m_0$)</th>
<th>$\mu_e$ ($10^3$ cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\mu_h$ ($10^3$ cm$^2$ V$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>7.99</td>
<td>90.27</td>
<td>3.02</td>
<td>0.52</td>
<td>1.23</td>
<td>4.03</td>
<td>0.139</td>
<td>0.438</td>
</tr>
<tr>
<td>6.92</td>
<td>2.80</td>
<td>7.91</td>
<td>89.36</td>
<td>3.02</td>
<td>0.52</td>
<td>0.20</td>
<td>6.37</td>
<td>5.306</td>
<td>0.173</td>
</tr>
<tr>
<td>7.50</td>
<td>3.29</td>
<td>7.90</td>
<td>89.57</td>
<td>3.02</td>
<td>0.52</td>
<td>0.22</td>
<td>5.23</td>
<td>4.430</td>
<td>0.257</td>
</tr>
<tr>
<td>8.18</td>
<td>3.91</td>
<td>7.89</td>
<td>89.83</td>
<td>3.02</td>
<td>0.52</td>
<td>0.25</td>
<td>5.00</td>
<td>3.495</td>
<td>0.283</td>
</tr>
<tr>
<td>9.00</td>
<td>4.73</td>
<td>7.88</td>
<td>90.22</td>
<td>3.02</td>
<td>0.52</td>
<td>0.31</td>
<td>5.72</td>
<td>2.242</td>
<td>0.217</td>
</tr>
<tr>
<td>10.00</td>
<td>5.84</td>
<td>7.87</td>
<td>91.04</td>
<td>3.02</td>
<td>0.52</td>
<td>0.44</td>
<td>63.98</td>
<td>1.110</td>
<td>0.002</td>
</tr>
<tr>
<td>11.25</td>
<td>7.39</td>
<td>7.86</td>
<td>92.33</td>
<td>3.02</td>
<td>0.52</td>
<td>0.87</td>
<td>0.65</td>
<td>0.282</td>
<td>17.053</td>
</tr>
</tbody>
</table>