

## Phosphorene Nanoribbons for Next-Generation Energy Devices

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### Introduction

The global energy demand is expected to double by 2050 and the escalating impacts of warming demand an urgent reduction in emissions. While sunlight is our most valuable renewable resource, the produced energy must also be efficiently stored and used. For this, concepts such as Power-to-X could harness intermittent renewable energy and convert it into other energy carriers ('X') for direct use, chemical synthesis and storage. A ubiquitous commonality among such future technologies is the requirement for new, high-performing and sustainably-produced materials. Among the next-generation materials being developed, those with nanoscale dimensions are receiving particular attention. For example, sheet-like 2-dimensional (2D) materials, can possess a range of bandgaps, high excitonic lifetimes, high theoretical charge storage capacity, and large surface areas.<sup>1</sup> Moreover, such properties can be combined with those of other materials in hybrid functional membranes, films, devices, and composites for a range of technologies.

While 2D nanomaterials are widely studied in sheet form, their ribbon analogues offer further unique and tuneable properties that derive from width-induced confinement and edge effects. Ribbons also offer different architectures for incorporation into applications. For these reasons, graphene nanoribbons (GNRs) have emerged as a major field of study; however, nanoribbons of other materials are far less common, mainly due to challenges in their synthesis. In 2019 we demonstrated the first isolation of discrete nanoribbons of phosphorene<sup>2</sup> (the 2D form of layered material black phosphorus, bP). Our work followed >100 theoretical papers predicting such phosphorene nanoribbons (PNRs) to have unique and superlative properties, which could translate to transformative benefits for many applications, especially those focused on green energy.<sup>3</sup>

### What are Phosphorene Nanoribbons?

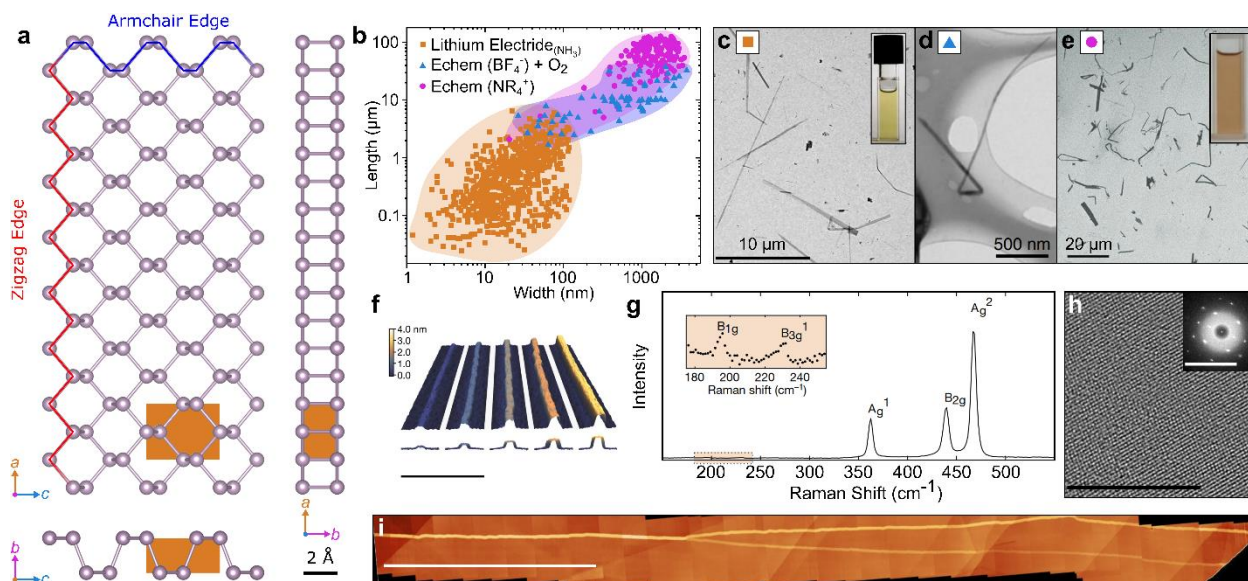
The structure of PNRs is shown in Figure 1a. Unlike graphene, the in plane atomic structure of phosphorene is highly anisotropic resulting in different properties in different crystallographic directions. Considering PNRs cut from the 2D sheets, the two structural extremes are 'zigzag' z-PNRs with edges parallel to the ridges and 'armchair' a-PNRs with edges parallel to the c-axis. The ribbon width and its uniformity are critical parameters for PNRs. Generally, the properties that are distinct from 2D sheets, only emerge from ribbons with widths below ~20 nm and the width variation needs to be small for these properties to be well-defined. The length of the ribbon is ideally >100 nm to avoid length-induced confinement and aid device assembly. For species with both in-plane dimensions of <100 nm, the additional confinement leads to formation of quasi-0D phosphorene quantum dots (PQDs).<sup>4,5</sup>

Phosphorene itself is well-studied due to its layer-number-dependent direct band gap (1.88eV vs bP 0.3eV), very high carrier mobility (310cm<sup>2</sup>/Vs), flexibility, surface area, and high theoretical capacity

for ion storage in the context of batteries.<sup>6</sup> PNRs are expected to emulate these advantages as well as dramatically increased tunability from the width, chirality, and edge structure/chemistry. For example, while phosphorene has a fixed bandgap, the diverse family of PNRs provides thousands of distinct structures, in theory allowing a single PNR type to be selected to provide a targeted band structure. For hydrogen-terminated PNRs, the band gaps have been predicted to be linked to the PNR width tending towards phosphorene at larger widths.<sup>7</sup> However, other predictions on non-edge terminated PNRs predict insulating a-PNRs and metallic z-PNRs. Beyond band gap engineering, PNRs have been predicted to host a range of exotic phenomena inaccessible to 2D phosphorene, including spin-density waves, room-temperature magnetism, topological phase transitions, large exciton splitting, and spin-dependent Seebeck coefficients.<sup>3</sup> Additionally, as quasi-1D objects, PNRs allow additional hierarchical architectures in comparison to 2D phosphorene, including nano/mesoporous assemblies, nematic liquid crystals, and uniaxial fibres. Collectively, these properties present a unique family of materials ideally placed to forge a wide range of next generation devices.

Since the first demonstration of isolated, discrete PNRs<sup>2</sup>, which followed attempts using lithography from bP/phosphorene, several synthetic approaches have been developed to create bulk PNR samples. Initially, we used 'ionic scissoring' submerging bP crystals in a lithium or sodium electride ammonia solution, forming  $\text{LiP}_x$  or  $\text{NaP}_x$  intercalation compounds which dissolve as anionic PNRs and metal counterions.<sup>2</sup> The ribbons are predominantly monolayer, typically 5-100 nm wide and typically 0.1-1  $\mu\text{m}$  long (although with measured ribbons up to 75  $\mu\text{m}$ ). Subsequent alternate routes have similarly involved intercalation of bP but via more readily-accessible electrochemical routes: reductive  $\text{NR}_4^+$  intercalation<sup>8</sup> for direct ribbonisation, or oxidative  $\text{BF}_4^-$  intercalation followed by  $\text{O}_2$  ribbonisation.<sup>9</sup> However, these electrochemical routes currently give significantly wider PNRs with a higher percentage of multi-layer species than electride synthesis (Fig 1b-e), providing a lower degree of confinement and properties closer to bP and/or phosphorene.

To date, all syntheses based on intercalation, exclusively produce z-PNRs, with the longer P-P bonds separating the atomic corrugations, breaking. The edge chemistry is unconfirmed and likely to vary between approaches. Electrochemical routes have been inferred to consist of various metastable P-O structures, while excess electrons from lithium electride synthesis makes local charges on edge-P likely. While the experimental field is currently in its infancy, initial results have encouragingly supported the superlative theoretical predictions of hole mobility, on/off ratio, flexibility, capacitance, and n/p-type behaviours.



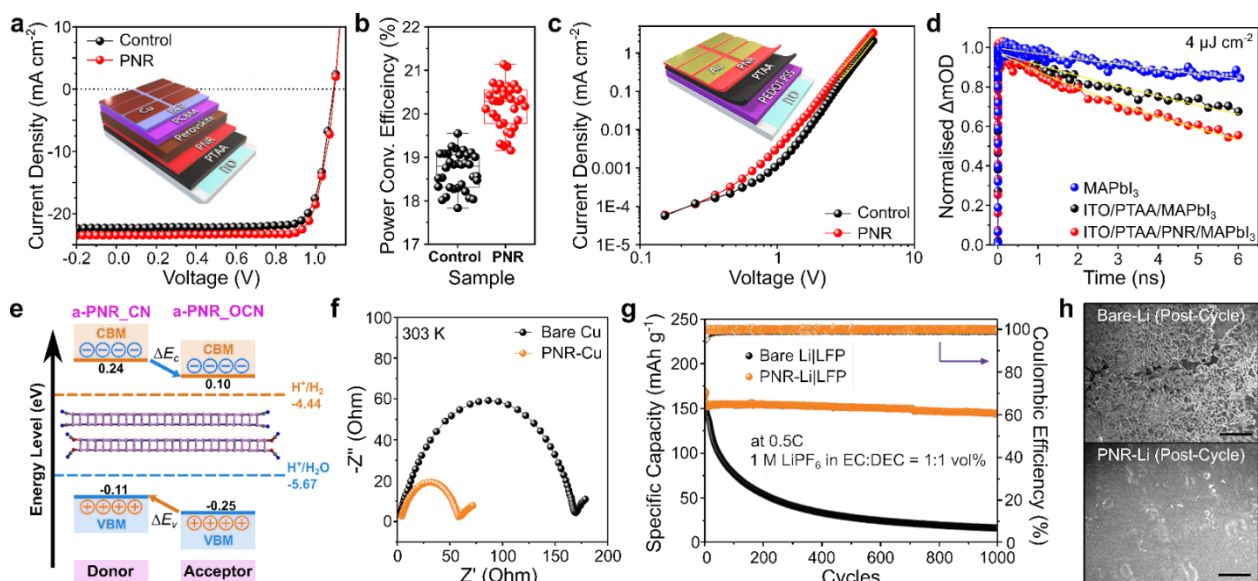
**Figure 1.** (a) Structure of PNRs down 3 crystallographic axes, with unit cell highlighted in orange and edge-types labelled. (b) PNR length and width distributions from current syntheses; Birch reduction (Watts et al.<sup>2</sup>), Cathodic electrochemical unzipping (Yu et al.<sup>8</sup>) and cathodic electrochemical intercalation followed by molecular oxygen unzipping (Liu et al.<sup>9</sup>). (c-e) TEM micrographs of PNRs synthesized from current syntheses with symbols linking to 1b and digital photographs of solutions inset. (f) AFM of 1-5 layer PNRs, scale bar 500 nm. (g) Raman spectrum of PNRs showing basal plane  $A_g^1$ ,  $B_{2g}$  and  $A_g^2$  modes, and edge-derived  $B_{1g}$  and  $B_{3g}^1$  modes with region magnified and highlighted. (h) High resolution TEM micrograph of PNR basal plane with selected area electron diffraction inset, scale bars 1nm/10nm<sup>-1</sup>, respectively. (i) AFM micrograph of monolayer PNR bifurcating from a few-layer PNR, scale bar 5 $\mu$ m. (c,g-i) Adapted with permission from Watts et al.<sup>2</sup> (d) Adapted from Liu et al.<sup>9</sup> under CC-BY 4.0. (e) Adapted with permission from Yu et al.<sup>8</sup>

## Energy Application of Phosphorene Nanoribbons

Despite their recent synthesis, PNRs have already been investigated in multiple energy devices. Of particular interest are PNRs' ultrahigh hole mobilities, which could be used to significantly benefit devices such as solar cells. Photovoltaics require both electron and hole transport layers (HTLs) with the latter currently one of the major bottlenecks to further enhancing the performance of emergent perovskite solar cells (PSCs). Most successful HTLs in high performance PSCs contain hygroscopic or corrosive dopants which hinders the overall device stability.<sup>10</sup> We recently provided the first example that the predicted superlative properties of PNRs discussed in theoretical studies translates to improved performance in a device.<sup>11</sup> These first PNR optoelectronic devices explored their exciting potential by achieving world-class efficiencies as a result of improved hole extraction; one of the key properties predicted by theorists. Figure 2a shows a current-voltage ( $J$ - $V$ ) curve for PSCs incorporating PNRs as a charge-selective interlayer enhancing hole extraction from the polycrystalline perovskite absorber, methylammonium lead iodide (MAPbI<sub>3</sub>), to the poly(triarylamine) (PTAA) semiconductor which is typically used alone as the HTL. The planar inverted PSCs achieved fill factors above 0.83 and efficiencies exceeding 21%. Such high efficiencies are typically only reported in single crystalline MAPbI<sub>3</sub>-based inverted PSCs. Over a large sample size as depicted in Figure 2b, PSCs incorporating PNRs showed significantly improved efficiencies in contrast to the devices without PNRs. In order to verify that the improved hole mobility was intrinsic to the PNRs and not limited to devices incorporating a perovskite absorber layer, hole-only space charge-limited current (SCLC) devices were also fabricated, which demonstrated a marked improvement in hole mobility for devices incorporating PNRs (Figure 2c). The experimentally-verified enhanced hole mobility in both PSCs and SCLC devices, demonstrate the PNRs' potential in universal optoelectronic applications. In the same study, we demonstrate more effective carrier extraction by virtue of device photoluminescence spectroscopy and by probing the charge transfer dynamics using femto-second transient absorption spectroscopy, faster decay kinetics were measured, indicative of faster hole extraction (Figure 2d). The use of PNRs here builds on an emerging field of phosphorene in PSCs, however, the tuneable optical properties of PNRs allows better tuning of band-level alignment, while the quasi-1D morphology allows percolating networks to be assembled from the liquid phase with limited restacking, unlike 2D species. We also note that to date, our PNR devices have demonstrated significantly higher efficiencies than any other phosphorene-based PSC. This first example of PNRs in optoelectronic devices opens up new avenues for future theoretical and alternative experimental applications by further exploiting their bandgap and/or edge states to suit a range of energy applications. One likely early optoelectronic candidate beyond PSCs is metal-free photocatalysis, where the carrier mobilities and strong visible light absorption make PNRs appealing materials for applications such as water splitting. The edge-chemistry-dependent band-structures of PNRs theoretically allows control over the band edge positions (Figure 2e), enabling the formation of

PNR heterostructures capable of photocatalyzing reactions fundamentally inaccessible to 2D phosphorene.<sup>12</sup>

Another major potential use of PNRs is in energy storage devices. High performance batteries require high volumetric and gravimetric energy densities, long cycle life, and power capabilities suited to the end user application. Phosphorous/phosphorene has a high theoretical ion storage capacity translating to 2596 mAh/g for lithiated phases<sup>6</sup> with stoichiometry  $\text{Li}_3\text{P}$  and has been shown as a functioning anode for several beyond-lithium metal-ion battery chemistries (Na, K).<sup>13</sup> As with most battery materials, the capacities achieved experimentally fall short of the theoretical value and performance. Firstly, the semiconducting nature of bP-derived materials necessitates the use of a carbon additive which decreases the practical energy density of the electrode (reported capacities of 2000 mAh  $\text{g}^{-1}$  are normalized to phosphorus content). Secondly, poor cycle life remains a pressing issue with papers rarely reporting 80% capacity retention beyond 100 cycles, attributed at least in part to the large volume changes of phosphorous on lithiation and delithiation which mechanically pulverises the electrode. Thoughtful design of electrodes built around nanosized phosphorus has been shown to be a promising route, which PNRs are well placed to exploit, as quasi-1D species alongside the 2D phosphorene and 0D PQDs together provide a range of dimensionalities to design and assemble P-rich anode architectures. Further, PNRs share phosphorene's very low barrier to Li diffusion in the zigzag direction (calculated at  $\sim 0.10$  eV) and a contrastingly high barrier to diffusion in the armchair direction.<sup>13</sup> The edge-rich nature of PNRs has also been exploited as a lithium-anode passivation layer.<sup>8</sup> The direct addition of PNRs onto lithium dramatically reduced the interfacial resistance (Figure 2f, 165.2  $\Omega$  to 54.6  $\Omega$ ) as it forms a  $\text{Li}_3\text{P}$ -rich phase; edge-deficient phosphorene was not as effective. The PNR-coated anodes implemented in  $\text{LiFePO}_4|\text{(PNR-)}\text{Li}$  batteries showed dramatically improved performance and stability (Figure 2g), with the lithium surface stabilized from roughening and dendrite formation during lithium plating and stripping (Figure 2h).



**Figure 2.** PNR devices. (a) PNR-modified perovskite solar cell  $J$ - $V$  curve with schematic inverted-device stack inset. (b) Efficiency of perovskite solar cells with and without PNR hole-transport layer,  $N=70$ . (c)  $J$ - $V$  plot of hole-only space charge-limited conduction devices with and without PNRs, with device architecture inset. (d) Decay kinetics of photobleaching measured by transient absorption spectroscopy of MAPbI<sub>3</sub> perovskite intrinsically, and on indium tin oxide/poly(triarylamine) with and without PNRs. (e) Schematic of edge-functionalized (nitrile/cyanate ester) a-PNR heterobilayers as solar water splitting cells, with energy of conduction/valence band maxima (C/VBM) referenced versus redox potentials. (f) Electrochemical impedance spectra of bare Li and PNR-Li on Cu, showing lower interfacial resistance with PNRs (g) Galvanostatic cycling performance of  $\text{LiFePO}_4|\text{Li}$  full-cell

battery with/without PNR protective layers (h) SEM micrographs of post-cycling anode surface showing Li surface without (top) and with (bottom) PNRs preventing dendrite formation, scale bars 50  $\mu\text{m}$ . (a-d) Adapted with permission from Macdonald et al.<sup>11</sup> (e) Adapted with permission from Hu et al.<sup>12</sup> (f-h) Adapted with permission from Yu et al.<sup>8</sup>

## Challenges and Opportunities for Phosphorene Nanoribbons

Realizing the promise of PNRs requires workable quantities of homogeneous ribbons, ideally with <20 nm widths required to access the superlative optoelectronic properties. However, current top-down PNR syntheses through bP-ribbonization produce a polydisperse distribution of z-PNR widths and lengths. The width distribution is dictated to a certain degree by the primary synthesis approach (Fig 1b), and additional processing will allow further control, e.g. sonication in solvent after electride synthesis leads to narrower distribution of widths.<sup>2</sup> These polydisperse samples can potentially be “sorted” for specific applications that may require well-defined optical/electronic properties via techniques analogous to those developed for carbon nanotubes, although the challenge will be amplified by the air/moisture instability of phosphorene materials. For future real-world use, PNR synthesis itself must also be scaled and although current methods have their limitations, encouragingly they are intrinsically scalable. However, new, greener synthetic approaches would provide major breakthrough for PNR research. Regardless, the top-down routes also require high-quality precursor bP, which is presently only produced in gram batches (limiting current PNR syntheses to the sub-gram scale), although more scalable syntheses are currently being reported from red phosphorus, which is produced on the megaton scale.<sup>6</sup> Moving forward, bottom-up production routes hold promise, with early chemical vapour deposition synthesis providing high aspect ratio bP with sub-micron widths.<sup>14</sup> Bottom-up synthesis could conceptually provide monodisperse PNRs with control over width, edge chemistry, chirality (e.g. armchair PNRs), presenting a rich area for synthetic research.

In addition to width/chirality control, the optoelectronics may be tenable through functionalization of the phosphorus framework, with the modification's chemistry, stoichiometry, and locus providing significant parameter space to dictate PNR properties. Classic covalent-nanomaterial reactions, including diazonium, cycloadditions, and reductive chemistries are likely early candidates, and the rich history of phosphorus chemistry will provide unique avenues for investigation. The air-stability of PNRs is an open question. The oxidation and degradation of the phosphorene basal plane appears to be absent in PNRs, but initial observations indicate slow PNR oxidation from the edge,<sup>2</sup> so edge-specific functionalization may prove a promising route to curtail PNR degradation. The abundance of edge states and confinement-derived tuneable band structure is shared between PNRs and PQDs, and it is envisioned that many tools, chemistries and applications of each are likely to overlap. Currently however, the zigzag-only unzipping of existing PNR syntheses leads to more homogeneous samples than existing PQD production routes.<sup>5</sup>

## Bright Future for Phosphorene Nanoribbons

PNRs are well placed to enhance a number of next generation energy devices, coupling the intrinsic properties of phosphorene with the far greater tunability intrinsic to nanoribbons. Initial work confirms their promise in PV and battery devices, and further work will continue to push the boundaries in these areas, but potentially greater promise can be seen in the exotic theorized physical properties. Novel magnetism and edge spin states could lead to advances in spintronics and

energy efficient memory storage and is expected to be a major area of research. The solution-processability of PNRs is a significant benefit which has accelerated much of the early device work, and development of targeted functionalisation chemistries will not only improve processability further but could provide the toolset to dictate PNR properties.

These advances are contingent on more widespread availability of PNRs, and advances in synthesis will be key, with the cost and availability of black phosphorus likely the key hurdle for top-down approaches beyond scientific research. Economically, the phenomenal properties of PNRs, and associated device value, coupled to the natural abundance of phosphorus makes for a compelling case, so industrial uptake and investment could be swift.

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