

# Scalable Topochemical Synthesis of Black Phosphorene Nanoribbons

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**ABSTRACT:** Black phosphorene nanoribbons (PNRs) are unique quasi-1D nanomaterials that have attracted enormous interest due to their properties, such as tunable bandgap, magnetism, and semiconducting ground states at room temperature. However, the scalable synthesis of PNRs has remained a considerable challenge. We report the scalable topochemical synthesis of PNRs by the solid lithiation of black phosphorus (BP) powder and subsequent exfoliation into nanoribbons. The produced PNRs have an average length of 3.48  $\mu\text{m}$ , an aspect ratio up to 137, a minimum thickness of 5 layers for individual nanoribbons, and an average thickness of 14 layers. This method has a high yield of 61%, a powder production scale of 10 g, and a liter-range colloidal dispersion. The PNRs can be easily processed into versatile, flexible devices on a fabric substrate by screen printing. A cellulose/(DMF-dispersed PNR) (Cel/D-PNR) flexible film has excellent flame-retardant properties, with a limiting oxygen index (LOI) reaching 33%. PNR-supported Co nanoparticles ( $\text{Co}_x\text{-PNR}$ ) had an outstanding oxygen evolution reaction (OER) performance with an overpotential of only 350 mV at 10  $\text{mA}/\text{cm}^2$ . This work allows the scalable production of PNRs in order to explore their potential applications in flexible electronics and energy conversion.



## INTRODUCTION

Nanoribbons are quasi-1D strips with widths ranging from 1 to 100 nm,<sup>1,2</sup> which have attracted tremendous attention due to their electronic, optical, and chemical properties governed by quantum confinement and edge states.<sup>3–8</sup> Graphene nanoribbons have been frequently studied for their spin-ordered electronic states due to their structural rigidity, electronic tunability, weak spin–orbit coupling, and surface compatibility.<sup>6,9–11</sup> PNRs are single-element materials characterized by room temperature ferromagnetism.<sup>3</sup> Furthermore, they are predicted to possess properties including direct-band gap semiconductivity,<sup>12</sup> high carrier mobility and biocompatibility.<sup>13–15</sup> These properties make them a unique material for studying key scientific issues in fundamental physics and make them useful for fields such as flexible electronics,<sup>16</sup> catalysis,<sup>17,18</sup> and energy storage.<sup>19,20</sup> These applications require large quantities of PNR dispersions or powder, but their scalable synthesis remains challenging.

BP belongs to the orthorhombic crystal system, in which atoms within each layer are covalently bonded to form a wrinkled two-dimensional honeycomb structure. Each phosphorus atom bonds with three neighboring atoms, giving rise to two characteristic orientations: the armchair (AC) and zigzag (ZZ) directions. The preparation of BP crystals into nanoribbons requires the use of force to overcome the van der Waals forces between layers and to cut in the zigzag (ZZ)

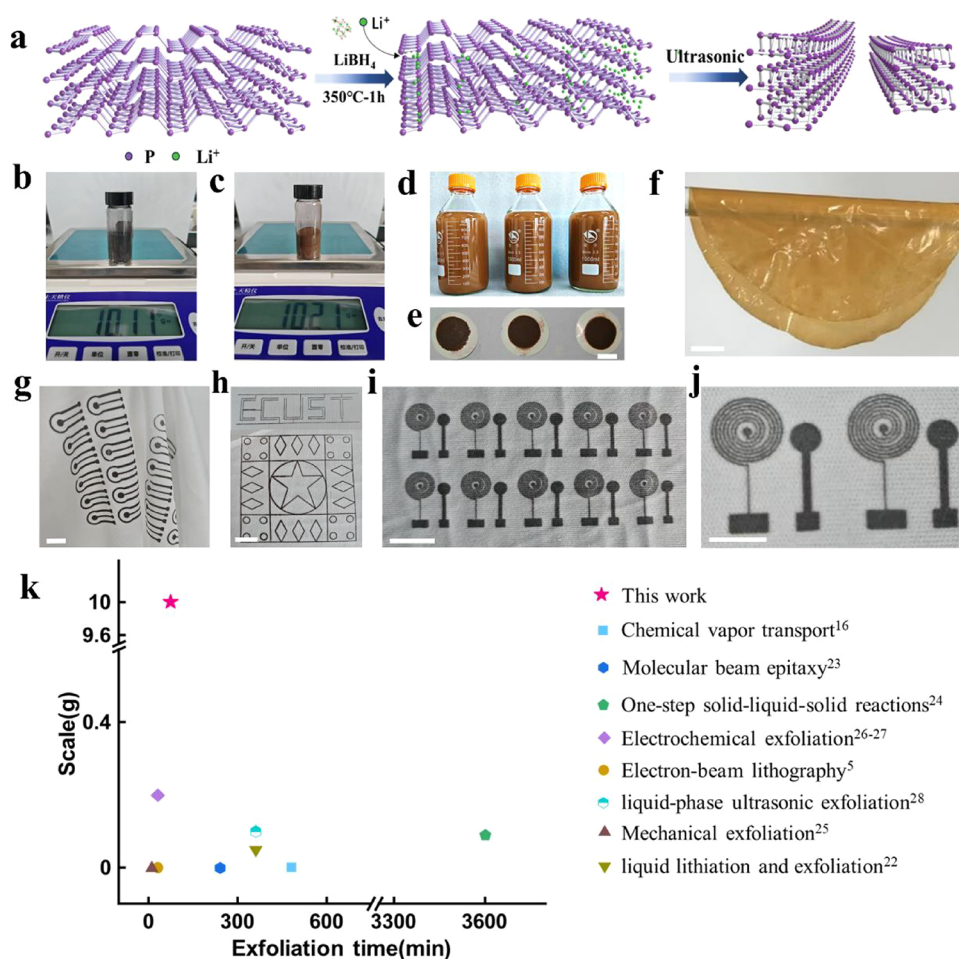
direction to form ribbons in nanoscale width.<sup>21,22</sup> At present various bottom-up and top-down methods have been used to synthesize PNRs. The bottom-up methods are mainly divided into chemical vapor transport (CVT),<sup>16</sup> molecular beam epitaxy and one-step solid–liquid–solid reactions.<sup>23,24</sup> The CVT method used for the growth of PNR arrays or thin films requires BP nanoparticles as seeds. The resulting nanoribbons are uniform and of high quality, but their growth rate is slow, making large-scale production difficult.<sup>16</sup> The atomic precision of molecular beam epitaxy is unmatched by traditional manufacturing methods, but its complexity and dependence on substrates limit its use.<sup>23</sup> Although the one-step method features operational simplicity, it suffers from low time efficiency. Moreover, the use of bismuth as a flux introduces impurities into the nanoribbons, which further requires additional purification procedures.<sup>24</sup> Top-down methods include mechanical,<sup>25</sup> electrochemical exfoliation,<sup>26,27</sup> electron-beam lithography,<sup>5</sup> liquid lithiation and exfoliation and liquid-phase ultrasonic exfoliation.<sup>22,28</sup> Mechanical exfoliation

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**Figure 1.** Scalable topochemical synthesis of PNRs and PNR ink. (a) Schematic of the topochemical synthesis of PNRs. (b) Photograph of BP bulk powder. (c) Photograph of PNRs. (d) Photograph of solutions of PNRs (0.3 mg/mL) dispersed in deionized water. (e) A PNR membrane. Scale bar, 10 mm. (f) Cel/D-PNR composite film. Scale bar, 10 mm. (g–j) Various screen-printed patterns on nonwoven fabric using PNR ink. (g) Serial polka dots, Scale bar, 10 mm. (h) Star map and ECUST logo, Scale bar, 10 mm. (i) A flexible disc electrode pressure sensor, with (j) an enlarged view of (i). Scale bar, 10 mm. (k) Exfoliation time versus production scale of PNRs prepared by different methods. Superscript numbers are the reference numbers.

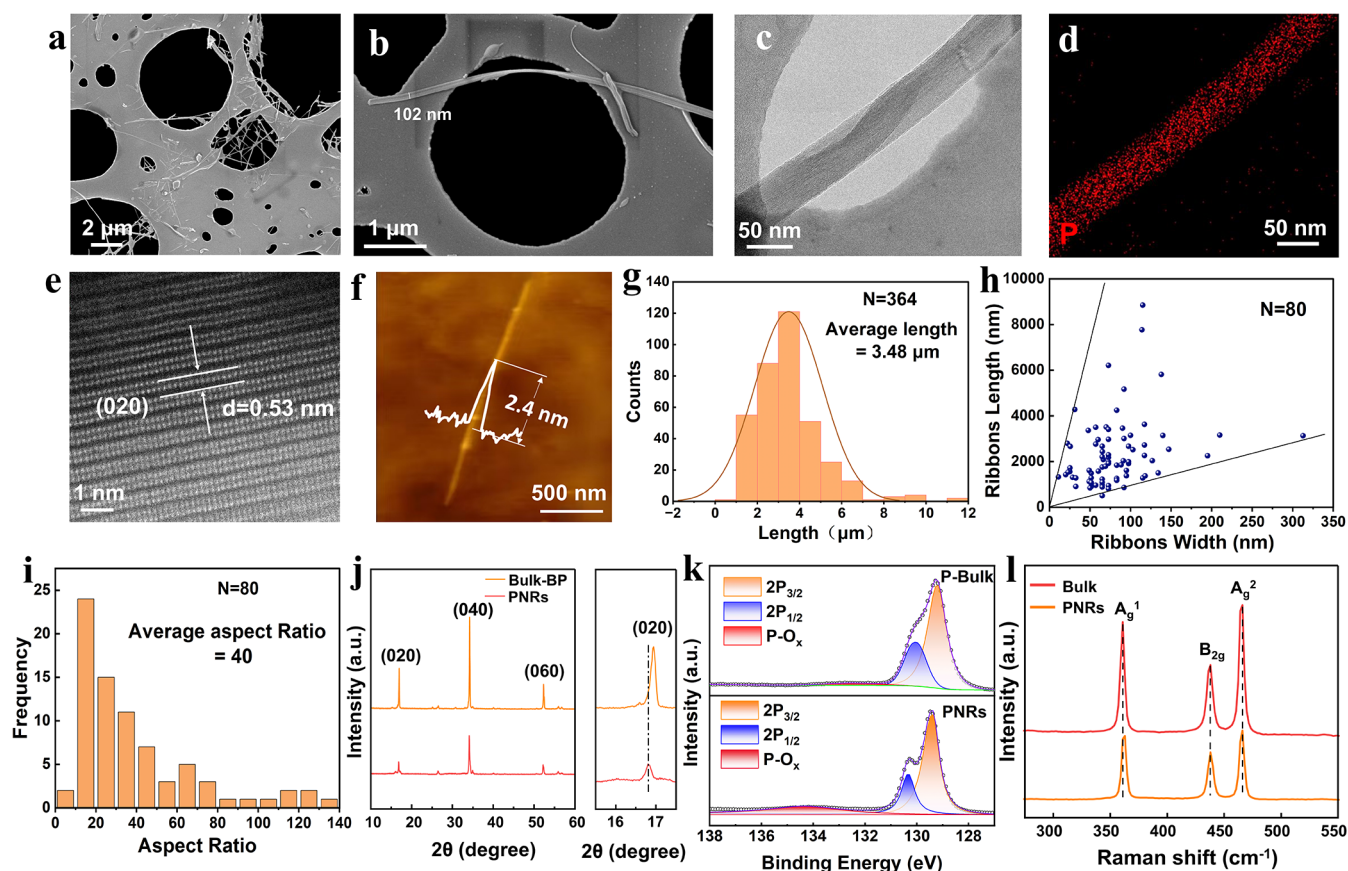
predominantly overcomes the interlayer bonding in BP by shear force, but its low yield prevents the scalable production of freestanding PNRs.<sup>25</sup> Compared with other exfoliation techniques, electrochemically exfoliated PNRs are susceptible to oxidation and are limited to milligram scale production. Liquid lithiation and exfoliation has been reported to produce monolayer PNRs, however, it is relatively complex due to the use of explosive lithium metal in liquid ammonia, time-consuming, and requires a low temperature of  $-50\text{ }^{\circ}\text{C}$ ,<sup>22</sup> making economical scale-up difficult. Despite the fact that liquid-phase ultrasonic exfoliation gives a high yield (95%), its long processing time and small-scale production limit its use.<sup>28</sup> As a result, the large-scale production of PNRs remains a considerable challenge in the fields of energy catalysis and polymer composites, where the demand for materials is high.

In this work, we achieve Lithium ions insertion through a topochemical method and subsequently exfoliate the material into nanoribbons using probe ultrasonics. The nanoribbons exhibit widths ranging from 20 to 120 nm, with an average length of  $3.48\text{ }\mu\text{m}$  and an average thickness of 6.9 nm. Furthermore, the yield can reach up to 61% in DMF solvent. This process enables the preparation of 10 g of PNR powder. Experimental studies have demonstrated that optimal inter-

calation is achieved at a Li/P molar ratio of 0.125. Density functional theory (DFT) calculations reveal that this ratio yields the lowest formation energy of the system ( $-0.08361\text{ eV}$ ) and the lowest adsorption energy for lithium ions intercalating along the Z–Z direction. These intercalated lithium ions preferentially weaken and break the longer P–P bonds, thereby facilitating the subsequent ultrasound-assisted sonication formation of PNRs. PNRs possess a wide range of potential functional applications. We demonstrate the exceptional flame-retardant properties of PNRs, with Cel/D-PNR flexible film exhibiting a limiting oxygen index (LOI) of 33%.  $\text{Co}_x\text{-PNR}$  also exhibit outstanding OER performance, with an overpotential of only 350 mV at  $10\text{ mA/cm}^2$  and stable cycling for 100 h at  $100\text{ mA/cm}^2$ , demonstrating excellent catalytic activity and cycling stability. This method provides material support for both flame retardancy and electrocatalysis applications.

## RESULTS AND DISCUSSION

We report a scalable topochemical method for synthesizing high-quality PNRs (Figure 1a), which uses  $\text{LiBH}_4$  as a solid intercalant to complete Li ion intercalation, followed by the liquid-phase exfoliation of BP to produce PNRs. We

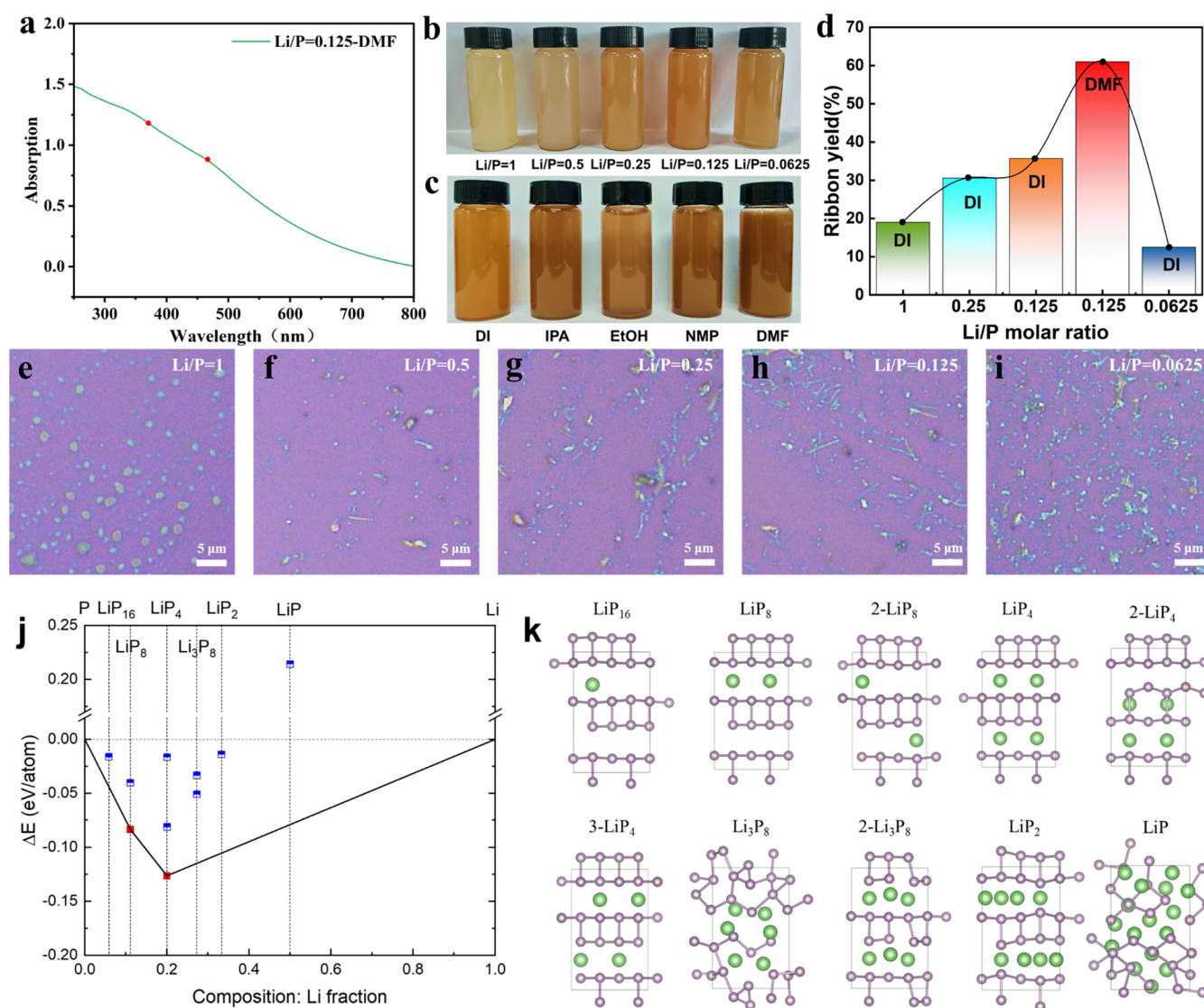


**Figure 2.** Morphology and structural characterization of PNRs. (a) SEM image of PNRs dispersed on a copper mesh. (b) Magnified image of two nanoribbons in (a). (c) TEM image of a PNR. (d) EDS determination of P in the area in (c). (e) HAADF-STEM image of a PNR. (f) AFM image of a PNR. (g) PNR length distribution. (h) Width and length distributions and (i) aspect ratios of PNRs. (j) XRD pattern of PNRs. (k) XPS spectra of BP and PNRs. (l) Raman spectra of BP and PNRs.

investigated the molar ratio of  $\text{LiBH}_4$  to BP crystals and lithium intercalation time and found that the best exfoliation efficiency was achieved at a Li/P molar ratio of 0.125 with 1 h intercalation time. The method is scalable and 10 g PNR powder was produced (Figure 1b,c), an achievement that no previously reported method has been able to achieve. Brown-colored stable PNR dispersions in a liter scale were also produced, which could be used to produce films supported on a nylon substrate and flexible Cel/D-PNR film (Figure 1d–f). The PNR powder has excellent processability, enabling the development of inks for producing versatile micropatterns by screen printing, including serial polka dot sensors, an “ECUST” logo, stars, and a flexible disc electrode array pressure sensor, suggesting its potential use in the large-area, low-cost patterned manufacturing of flexible electronics (Figure 1g–j). Figure 1k shows a comparison of the efficiency of solid-phase lithiation and other methods for the production of PNRs, such as molecular beam epitaxy, electrochemical and mechanical exfoliation, electron-beam lithography, CVT, liquid-phase ultrasonic exfoliation, liquid lithiation and exfoliation, and solid lithiation exfoliation (Table S1). This reported method achieves the largest scale production in the shortest time and is the only known method that can achieve large-scale production in only 75 min.

The morphology and crystal structure of PNRs were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), and transmission electron microscopy (TEM). SEM images show the quasi-1D nanostructure of

PNRs, with widths ranging approximately from 20 to 120 nm and lengths from 2 to 10  $\mu\text{m}$  (Figure 2a). The single nanoribbon shown in Figure 2b had a length of approx 5.6  $\mu\text{m}$  and a width of 102 nm. The nanoribbons have a relatively uniform structure and are interwoven and entangled with each other, indicating excellent flexibility (Figure S1). A TEM image of the nanoribbons shows a uniform thickness, distinct edges, and a width of approximately 50 nm (Figure 2c). Energy dispersive spectroscopy (EDS) shows a relative uniform distribution of the P element, which is basically consistent with the TEM results (Figure 2d). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image shows that the interlayer spacing of the PNRs is approximately 0.53 nm (Figure 2e),<sup>29</sup> which corresponds to the crystal plane spacing of the (020) plane of BP crystals. The PNRs also have an obvious banded structure (Figure S2), and their diffraction patterns have clear spots and a high symmetry, indicating their good crystallinity and that the nanoribbons were not severely damaged during preparation (Figure S3). AFM image of a single PNR shows a thickness of 2.4 nm (approximately 5 layers) (Figure 2f), and a statistical analysis of 570 nanoribbons gave an average value of 6.9 nm (approximately 14 layers, Figure S4). An analysis of the lengths of 384 nanoribbons gave a narrow distribution with an average value of about 3.48  $\mu\text{m}$  while the average width was 80 nm (Figure 2g), giving a mean aspect ratio of approximately 40. The aspect ratio mainly in the range 20 to 40, indicating uniform length and width of PNRs (Figure 2h–i). X-ray



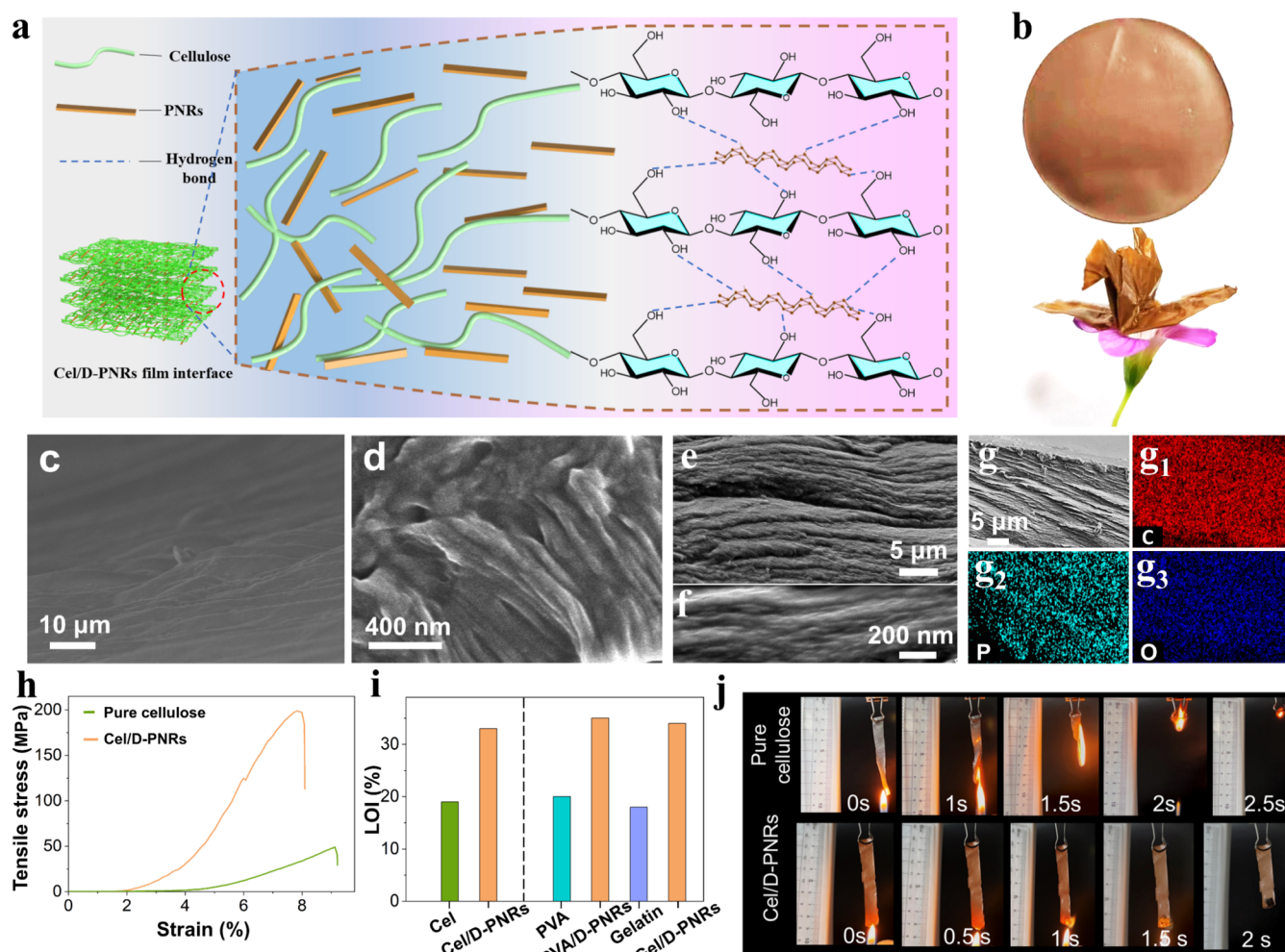
**Figure 3.** The topochemical exfoliation mechanism. (a) UV–Vis absorption spectrum of PNRs produced with an Li/P molar ratio of 0.125. (b) Photograph of PNRs in a deionized water solution prepared with different lithium intercalation parameters (Li/P = 1, 0.5, 0.25, 0.125 and 0.0625). (c) Photograph of PNRs dispersed in different solvents (DI, IPA, EtOH, NMP and DMF) prepared with a Li/P ratio of 0.125. (d) Yield of nanoribbons under different Li/P ratios and solvents. (e–i) LSCM images of PNRs prepared with different Li/P ratios (Li/P = 1, 0.5, 0.25, 0.125 and 0.0625) in a DMF solution. (j) Convex hull graph of formation energies for the Li–P binary system; Red indicates a stable structure, while blue indicates a metastable or unstable structure. (k) Adsorption site maps for different Li/P molar ratios (Li/P = 0.0625, 0.125, 0.25, 0.375, 0.5 and 1).

diffraction (XRD) patterns show that the peak positions for PNRs are almost the same as for bulk BP with a lower intensity, indicating that the PNRs contained few-layer structure. The (020) peak for PNRs is at a slightly smaller angle because of the insertion of Li which increases the interlayer spacing (Figure 2j).

Figure S5 shows the color changes in the solutions of DMF-dispersible PNRs and water-dispersible PNRs over a two-week period, with the DMF solution showing virtually no discernible change. The UV absorption spectra indicate a slight decrease in absorbance, proving the stability of PNRs in DMF dispersions. The Tyndall effect of the PNR colloid in DMF also shows the colloidal nature (Inset in Figure S5). To observe whether the PNRs undergo oxidation, BP and PNRs were analyzed using X-ray photoelectron spectroscopy (XPS) (Figure 2k). In the XPS spectrum of BP, the spin–orbit doublet peaks of  $P_{2p}$  correspond to  $2P_{3/2}$  (129.5 eV) and  $2P_{1/2}$  (130.3 eV), respectively, and there is no (P–O<sub>x</sub>) oxidation

signal at ~135 eV.<sup>22,27</sup> However, for the PNRs, a small oxidation peak appeared at 134–135 eV, indicating that they have undergone some oxidation. There are three characteristic peaks in the Raman spectra of PNRs with wave numbers of 362.6, 439.8, and 467.8  $\text{cm}^{-1}$ . The peak at 362.6  $\text{cm}^{-1}$  corresponds to the out-of-plane  $A_g^1$  phonon mode, while the peaks at 439.8  $\text{cm}^{-1}$  and 467.8  $\text{cm}^{-1}$  are respectively attributed to the in-plane  $B_{2g}$  and  $A_g^2$  phonon modes. The observed phonon modes of the PNRs are consistent with those reported for a bulk BP crystal.<sup>21</sup> Furthermore, the  $A_g^1/A_g^2$  ratio is greater than 0.5, indicating a high crystallinity (Figure 2l).<sup>25</sup>

We next examined the exfoliation of PNRs at different Li/P molar ratios and in different solvents, including deionized (DI) water, dimethylformamide (DMF), *N*-Methyl pyrrolidone (NMP), isopropyl alcohol (IPA) and ethanol (EtOH) by both analysis and simulation. The dispersion of PNRs in DMF and other solvents were examined to determine the optimal reaction condition. By comparing the UV–Vis absorption



**Figure 4.** Flame-retardant performance of Cel/D-PNR composite film. (a) Diagram of the cross-sectional structure of a PNR and cellulose composite film. (b) Photograph of a flat Cel/D-PNR film and thousand-film cranes prepared from it. (c) Top-view SEM image of the Cel/D-PNR composite film. (d) is an enlarged view of (c). (e) Cross-section SEM image of the Cel/PNR film. (f) is an enlarged view of (e). (g) Cross-section image of the Cel/PNR, ( $g_1$ – $g_3$ ) elemental maps of C, P and O in the Cel/PNR film. (h) Cel/D-PNR film tensile stress test. (i) LOI value of pure cellulose, Cel/D-PNRs, PVA, PVA/D-PNRs, gelatin, and Gel/D-PNRs. (j) Flame snapshot treatment of pure cellulose and Cel/D-PNR films. The images were captured from the video in [Movie S1](#) and [Movie S2](#).

spectra of the samples in different solvents (DMF, DI water) and at different molar ratios, it was found that the highest absorption was observed when the Li/P molar ratio was 0.125, which gave the highest concentration of PNRs. This also suggests that a Li/P molar ratio of 0.125 in DMF solution gives the best delamination with yield as high as 61% in DMF ([Figures 3a,d](#) and [S6](#)). We compared the changes of solution color with different concentrations of PNRs in the same solvent and the same concentrations in different solvents. Among them, the DMF solution shows a distinct brownish color ([Figure 3b,c](#)), indicating the highest concentration of nanoribbons, which is consistent with the UV–Vis results. Furthermore, laser scanning confocal microscopy (LSCM) ([Figure 3e–i](#)) diagram shows that, when the concentration decreases, the number of nanoribbons gradually increase. With a Li/P molar ratio of 0.125, the morphology of the PNRs shows a greater aspect ratio than to that at other ratios. When the ratio is decreased to 0.0625, the product contains a relatively large number of BP fragments and does not meet the definition for nanoribbons (aspect ratio ( $L/W$ )  $\geq 10$ ). [Figures S7](#) and [S8](#) show the morphology changes of the materials

produced using different Li/P molar ratios and solvents, from which it is clear that at a high Li/P molar ratio, excessive lithium intercalation leads to the production of phosphides and fragments. At a low Li/P molar ratio, the lithium intercalation is not sufficient to effectively strain and produce charge-driven effects within the crystal, making it difficult for the crystal to crack into nanoribbons. Furthermore, the PNRs produced in DMF are uniform in shape, slender, and thinner than those in deionized water ([Figure S8](#)). This is because DMF is a polar aprotic solvent with relatively stable chemical properties that does not undergo chemical reactions with the PNRs and produces structurally uniform nanoribbons. However, when the PNRs are dispersed in deionized water, the protons ( $H^+$ ) in the water react with the intercalated lithium to generate a large quantity of  $H_2$  bubbles. The collapse of these bubbles leads to the formation of irregular nanoribbons. Therefore, when Li/P is 0.125, the best exfoliation effect is achieved in a DMF dispersion. To investigate the optimal Li/P molar ratio of 0.125 for intercalation, we performed DFT calculations to evaluate the formation energies of PNRs at different Li/P molar ratios ([Table S2](#)). The results show that the formation

energy of the structure with a Li/P ratio of 0.125 is  $-0.084$  eV. This structure lies on the convex hull curve and possesses thermodynamic stability (Figure 3j,k and Table S2). Furthermore, to illustrate the mechanism underlying the lithiation-induced exfoliation process, we conducted ultrasonic treatments for different durations. We observed that after 1 min of ultrasonic treatment, a large number of nanoribbons were present on the surface of the bulk material. These are formed by the shearing of lithium ions. As the ultrasonic treatment continued, the nanoribbons were exfoliated from the surface of the bulk material, ultimately forming uniform, elongated PNRs (Figure S9). We also conducted a simulation of the adsorption sites of Li ion after intercalation (Figure S10(a–d)), calculating the adsorption energy of Li ion at different adsorption sites. The final simulation always results in the configuration shown in Figure S10d, indicating that there is only one stable adsorption position, and its adsorption energy is the lowest at 0.346 eV. The reason for this is that lithium ions are positioned along the ZZ direction in the BP. In this direction the P–P bond length is approximately 2.244 Å, while that in the AC direction is approximately 2.224 Å (Figure S11).<sup>30</sup> This means that the longer P–P bonds are weaker and cracks form along the ZZ direction. Then, through the cavitation effect generated by ultrasonic treatment, the BP crystals are exfoliated into nanoribbons (Figure S10e).

We also showed the potential applications of PNRs in various fields to demonstrate their versatility. We explored its fire-retarding properties for potential soft electronics applications. Considering their similar 1D topology, the PNRs were assembled with 1D cellulose nanofibers (CNFs) by vacuum filtration to freestanding Cel/D-PNR film (Figure 4a). As shown in Figure 4b, the film is lightweight and origami cranes crafted from Cel/D-PNR film are flexible and foldable. An SEM image of surface of a Cel/D-PNR film shows the radial alignment of both 1D nanomaterials (Figures 4c,d and S12). The cross-section of Cel/D-PNRs is macroscopically composed of 2D layers (Figures 4e,f and S13), with a homogeneous distribution of C, P and O (Figures 4g<sub>1</sub>–g<sub>3</sub> and S14). The van der Waals forces between the PNRs, together with the H-bonding with the CNFs allows the arrangement of layers stacked in the out-of-plane direction. This structure thus dramatically benefits mechanical reinforcement. As shown in Figure 4h, the tensile strength of the Cel/D-PNR film reaches  $\sim 200$  MPa, four times greater than that of a pure CNF film. The thermal stability is also greatly improved with less weight loss at the thermal degradation temperature of CNFs (Figure S15). Thus, both the mechanical and thermal properties of Cel/D-PNRs are much better than those of pure CNFs.

We also quantified the fire-retardant performance. As shown in Figure 4i, the introduction of PNRs increases the LOI of Cel/D-PNRs to 33%, a 74% increase over that of pure CNFs (19%). The PNRs can also be used in other polymeric composite systems involving poly(vinyl alcohol) (PVA)/D-PNR and gelatin (Gel)/D-PNR film, to give them high LOI values. This excellent fire resistance was verified by combustion tests (Figure 4j and the Supporting Information video of Movie S1 and S2). Pure CNFs undergo complete combustion in 2.5 s when contacting a flame, while the Cel/D-PNRs remain intact except for a small amount of ash at flame-contacting bottom. To further examine the effect of PNRs with different degrees of oxidation on flame-retardant properties, we prepared same size composite films by combining PNRs from the high-oxidation group (deionized water dispersed PNRs)

and the low-oxidation group (DMF-dispersed PNRs) with cellulose materials (Figure S16a,b), including cellulose films incorporating high-oxidation PNRs (Cel/W-PNRs) and low-oxidation PNRs (Cel/D-PNRs). The LOI values for Cel/W-PNRs and Cel/D-PNRs were 33 and 32% respectively. After combustion testing, Cel/W-PNRs retained shape well, indicating that oxidation had no effect on their flame-retardant properties; both exhibited excellent flame-retardant performance (Figure S16c,d and Supporting Information video of Movie S3). This outstanding fire-retardant performance is ascribed to the promotion of dehydration and carbonization of the CNFs by PNRs during combustion, which forms a dense carbonized layer that blocks the transfer of heat and oxygen. This layer also inhibits the release of combustible gases ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ), and phosphorus radicals directly capture combustion radicals, thereby acting as a flame-retardant.<sup>30–33</sup>

Because the PNRs have a high specific surface area and a high carrier mobility, we used a solvothermal method to combine them with cobalt. This method is particularly suitable for preserving the structural integrity of the PNRs while synthesizing cobalt-loaded PNRs that may be used in electrocatalysis, especially for reactions like the OER.<sup>34–39</sup> The EDS distribution map shows a relatively uniform distribution of Co, with distinct lattice fringes and diffraction spots, indicating that good crystallinity is maintained following the solvent-thermal reaction (Figure S17). The  $\text{Co}_x$ -PNRs have an outstanding performance in the OER, with an overpotential of only 350 mV at a current density of 10  $\text{mA}/\text{cm}^2$  and a Tafel slope of 109 mV/dec, comparable to the Tafel slope of commercial  $\text{RuO}_2$ , indicating rapid reaction kinetics. Electrochemical impedance spectroscopy reveals efficient charge transfer at the interface, demonstrating outstanding OER activity and kinetics. At a current density of 100  $\text{mA}/\text{cm}^2$ , the voltage remains essentially unchanged during extended cycling tests, proving its excellent electrocatalytic stability (Figure S18).  $\text{Co}_x$ -PNRs, therefore, have a great potential for use in electrocatalysis.

## CONCLUSION

In summary, we have developed a topochemical strategy for the scalable production of PNRs. Although this method enables the scalable production of PNRs, the process characteristics make it difficult to obtain high-quality monolayer structure directly. Consequently, this study strikes a reasonable balance between yield and material structural quality. The PNRs have excellent processability in the form of functional inks and solutions, highlighting their promise for applications such as flexible flame-retardant electronics. We demonstrate their utility in two distinct areas, including the well-known flame retardancy functionality and their relatively unexplored potential in OER catalysis. Beyond these examples, the expansion of PNRs into new application fields will depend critically on accessible mass production, a huge challenge this work directly addresses. Further, this present strategy may offer a generalizable route to synthesizing quasi-1D nanomaterials from other anisotropic layer materials.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.6c02221>.

Movie S1 shows the combustion of pure cellulose film in air (MP4)

Movie S2 shows the burning of Cel/D-PNR film in air (MP4)

Movie S3 shows the burning of the Cel/W-PNR film in air (MP4)

Experimental details, DFT calculations, Table, SEM, TEM, SAED, AFM, UV-vis, LCSM, and EDS characterization, electrocatalytic OER performance (PDF)

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### Notes

The authors declare no competing financial interest.

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