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Production of phosphorene nanoribbons

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Phosphorene is a mono-elemental two-dimensional (2D) material with outstanding, highly directional properties and a thickness-tuneable band gap[1-8]. Nanoribbons combine the flexibility and unidirectional properties of 1D nanomaterials, the high surface area of 2D nanomaterials and the electron-confinement and edge effects of both. Their structures can thus offer exceptional control over electronic bandstructure, lead to the emergence of novel phenomena and present unique architectures for applications[5,6,9-24]. Motivated by phosphorene's intrinsically anisotropic structure, theoretical predictions of the extraordinary properties of phosphorene nanoribbons (PNRs) have been rapidly emerging in recent years[5,6,12-24]. However to date, discrete PNRs have not been produced. Here we present a method for creating quantities of high quality, individual PNRs via ionic scissoring of macroscopic black phosphorus crystals.

25   **The top-down process results in stable liquid dispersions of PNRs with typical widths of**

26   **4 to 50 nm, predominantly single layer thickness, measured lengths up to 75 μm and**

27   **aspect ratios of up to ~1000. The nanoribbons are atomically-flat single crystals, aligned**

28   **exclusively in the zigzag crystallographic orientation. The ribbon widths are**

29   **remarkably uniform along their entire length and they display extreme flexibility.**

30   **These properties, in conjunction with the ease of down-stream manipulation via liquid-**

31   **phase methods, now enable the search for predicted exotic states[6,12-14,17-19,21] and an**

32   **array of applications where PNRs have been widely predicted to offer transformative**

33   **advantages, ranging from thermoelectric devices to high-capacity fast-charging**

34   **batteries and integrated high-speed electronic circuits[6,14-16,20,23,24].**

35

36   Phosphorene's anisotropic properties, including for electron, thermal and ionic transport,

37   derive from its atomic structure where the atoms are arranged in corrugated sheets with two

38   different P-P bond lengths (Fig. 1a)[1-8]. Calculations predict that PNRs can possess enhanced

39   characteristics compared with phosphorene and that their electronic structure, carrier

40   mobilities and optical and mechanical properties can be tuned by varying the ribbon width,

41   thickness, edge passivation, and by introducing strain or functionalization[6,12-14,20,22-24].

42   Additionally, there have been numerous predictions of exotic effects in PNRs, including the

43   spin-dependent Seebeck effect[17], room temperature magnetism[6,21], topological phase

44   transitions[18], large exciton splitting[14] and spin density waves[19]. These results have led to

45   suggestions of unique capabilities of PNRs in a number of applications such as thermoelectric

46   devices[6,23], photocatalytic water splitting[15], solar cells[14], batteries[6,24], electronics[6,20,22] and

47   quantum information technologies[14].

48

49   The production of nanoribbons of any material is a major challenge. Top-down processes

50   generally fail to deliver the narrow and uniform widths, crystallinity and crystallographic

51   alignment required for well-defined control of the nanoribbon's electronic structure[6,9,11,20].

52   Such control has been demonstrated by polymerisation of molecular precursors to produce

53   graphene nanoribbons (GNRs)[9], however, this and many other methods developed for

54   GNRs[10,11] are not currently transferable to phosphorene, an issue compounded by

55   phosphorene's air-sensitivity and chemical reactivity[6]. Attempts to fabricate PNRs have been

56   so far limited to etching of multi-layer black phosphorus (BP), the 3D layered parent

57   structure of phosphorene (Fig. 1a)[5,16,25]. Electron-beam sculpting produces nanoscale

58   constrictions over limited (< 15 nm) lengths rather than isolated nanoribbons[16]. Alternatively,

59   e-beam lithography has, to date, only produced ribbons with minimum widths of ~60 nm and

60   heights of ~3 nm (Ref 25) meaning their band gaps and electronic properties are close to

61   those of bulk BP[2,3,14,20,22]. Such lithography also relies on first exfoliating and then

62   crystallographically aligning BP, limiting the scalability essential for many applications.

63

64   Our method for PNR production follows a two-step process. First, macroscopic crystals of

65   bulk black phosphorus are intercalated with lithium ions via a low temperature, ammonia-

66   based method (Li:P molar ratio 1:8). The resulting compound is then immersed in an aprotic

67   solvent and mechanically agitated producing stable liquid dispersions of PNRs (Fig. 1b,

68   inset). A schematic of the process is shown in Extended Data Fig. 1 and further details are

69   given in the Methods. The mechanism for ribbon formation is discussed below. For

70   characterisation the PNRs were drop-cast from liquid dispersion onto graphite substrates or

71   Transmission Electron Microscopy (TEM) grids.

72

73

74   Following deposition, the TEM grids were ubiquitously covered in ribbons. Example

75   micrographs are displayed in Fig. 1b and a gallery of TEM images is shown in Extended Data

76   Fig. 2, which presents densely packed heterogeneous PNRs and isolated high aspect ratio

77   ribbons with widths < 5 nm. From TEM data, the length and width of 940 individual ribbons

78   were measured (Methods), plotted as a scatter plot in Fig. 1c. The average length of these

79   ribbons is 690 nm, average width 30 nm; 33% of the ribbons are narrower than 10 nm.

80   Histograms of the width and lengths with axes corresponding to the dashed rectangle in the

81   scatterplot are also shown in Fig. 1c.

82

83   Selected Area Electron Diffraction (SAED) was used to investigate the crystallinity of the

84   deposited ribbons. The TEM micrograph in Fig. 1d contains a ribbon of length ~11 μm. The

85   abrupt changes of the ribbon direction are a result of it twisting and folding onto the

86   continuous carbon TEM grid upon deposition. SAED patterns were taken at six different

87   locations along this ribbon (Fig. 1e and Extended Data Fig. 3) and each match the in-plane

88   black phosphorus diffraction pattern (Methods). Moreover, comparing the alignment of the

89   individual reciprocal space SAED patterns with their corresponding real space images reveals

90   that the long ribbon axis is always oriented in the zigzag crystallographic direction (as

91   indicated by red arrows in Figs. 1a, 1d, 1e, Extended Data Fig. 3). Equivalent measurements

92   were performed on over 40 PNRs and in all cases SAED confirmed that the PNRs were

93   crystallographically intact along their length and zigzag edge-aligned, with no other

94   alignment observed.

95

96   Ribbon folding upon drying could be reduced by using holey carbon TEM grids. In this case,

97   the PNRs were found to be extraordinarily flexible and could twist, loop and coil around the

98   carbon substrate as seen in Figs. 1f, 1g and Extended Data Fig. 2c. This flexibility, combined

99   with their low TEM contrast, indicates that the PNRs are only a few layers thick, though only

100   in rare cases could TEM be used to determine their height. Fig. 1g shows a high-resolution

101   TEM (HRTEM) image taken through a ribbon fold. For this ribbon, the intact atomic

102   corrugations of the BP lattice are visible and seven distinct layers can be counted. HRTEM

103   taken through the flat part of the ribbon (Fig. 1h) reveals the expected, in-plane BP lattice,

104   which give sharp spots in the associated Fast Fourier Transform.

105

106   To accurately measure the ribbon heights, we used high-speed atomic force microscopy (HS-

107   AFM) to obtain height-calibrated data over large areas of the substrate (Methods). In all

108   cases, the PNRs' heights closely matched an integer number of layers of black phosphorus.

109   Fig. 2a presents example HS-AFM images of 1 to 5 layer PNRs in 3D view and the same data

110   viewed through the length of each ribbon. These data demonstrate the remarkable height

111   uniformity of the PNRs along their length, showing no fragments or residual species

112   commonly found on AFM images of liquid exfoliated nanomaterials. To determine the PNR

113   heights and roughnesses with greater statistical accuracy, over 130 PNRs of up to five layers

114   thick were imaged and the heights of every pixel in each ribbon extracted and are plotted as

115   normalised histograms in Extended Data Fig. 4 (Methods). Gaussian fits to the histograms

116   determine the heights of 1, 2, 3, 4 and 5 layer PNRs to be 0.52, 1.04, 1.57, 2.09 and 2.74 nm

117   respectively. Notably, the overall roughnesses, which corresponds to the standard deviation

118   of the PNR heights, taken from fits to all measurements in each case (Methods, Extended

119   Data Fig. 4) are comparable to the equivalent data for the naked, atomically-flat graphite

120   substrate.

121

122   The PNR layer number distribution within a typical sample was estimated by analysing all

123   the ribbons deposited within a 300 x 300 μm square region on the HOPG substrate plotted in

124   Fig. 2b (Methods). These data show the majority of the PNRs are monolayer (~65%); 84%

125   were trilayer or fewer.

126

127   A high degree of width uniformity is required for nanoribbons with precisely defined

128   electronic character[6,9,11,20]. Fig. 2d displays a ~3 μm section from a single layer PNR. This

129   ribbon's width was measured at over 2,300 points along its length (Methods), plotted as a

130   histogram in Fig. 2c. A Gaussian fit determines the mean width to be 10.3 nm with a standard

131   deviation of 0.7 nm (Methods).

132

133   HS-AFM also enabled the study of the longest PNRs. Fig. 2e is a composite HS-AFM image

134   of a ribbon greater than 75 μm in length, alongside the corresponding gradient image

135   (Methods) to highlight the PNR position given its extreme aspect ratio; the ribbon is more

136   clearly visualised in Supplementary Video 1. This ribbon branches at several points along its

137   length, a phenomenon occasionally found for the longer ribbons (see also Extended Data Fig.

138   5). Line profiles (Extended Data Fig. 5) at the branching points (Fig. 2e, left) reveal that the

139   split is due to the multilayer ribbon having bifurcated via self-cleaving. The extreme

140   flexibility of the PNRs is again demonstrated; the ribbons both follow the underlying graphite

141   steps, or other PNRs when laying on top one another (Fig. 2e, right) with sub-nanometre

142   conformity.

143

144   We now discuss the mechanism of PNR formation. Control experiments (Methods) confirm

145   that the lithium intercalation step is essential for ribbon production. Metal-intercalation of

146   black phosphorus (BP) is not fully understood since attempts typically result in both

147   intercalation and other phosphorus-containing compounds, and a well-defined interlayer

148   increase, typical for intercalation compounds, is not found[26] (Methods). Recent HRTEM

149 experiments on BP intercalation[27] have confirmed the predicted extraordinarily rapid alkali

150 metal ion diffusion along the zigzag direction[8]. This process results in the metal atoms

151 forming 'stripes' along the corrugated channels of the BP crystal upon initial doping[27]. The

152 strain between the intercalated and unintercalated regions, combined with high local electron

153 doping, can cause the longer P-P bonds to break and thus crack formation in the zigzag

154 direction [8,26-28]. These findings are consistent with our own observations. Figs. 3a-c presents

155 TEM data capturing the three stages of ribbon formation: Fig. 3a shows a Li-intercalated BP

156 (Li-BP) flake exhibiting cracks along only one direction; Fig. 3b, a flake splitting along these

157 cracks; eventually leading to the formation of isolated ribbons upon mechanical agitation

158 (Fig. 3c). Alternatively, the PNRs were found to spontaneously dissolve from Li-BP crystal,

159 that is, without any agitation or reaction, similar to other nanomaterials when negatively

160 charged by intercalation[29]. The spontaneously dissolved PNRs were found to have greater

161 average width and length than those formed by mechanical agitation (Extended Data Fig. 6).

162

163 Applying an electric field to a PNR liquid dispersion (Methods), via Pt-coated electrodes,

164 demonstrates the negative charge on the PNRs in solution, since they are found to

165 electroplate only onto the metallic parts of the positive electrode, as confirmed by Raman and

166 XPS mapping (Fig. 3d-f, Extended Data Fig. 7, Methods). The PNR solutions were found to

167 be remarkably stable in inert atmosphere with UV/Vis absorption measurements,

168 demonstrating less than a 1.5% decrease in absorbance over 50 days (Extended Data Fig. 10,

169 Methods).

170

171 We therefore propose the following formation mechanism. The highly directional and rapid

172 intercalation of metal ions leads to breaking of longer P-P bonds along the zigzag direction,

173 resulting in ribbon-like fragments within the Li-BP crystal. The ion intercalation negatively

174 charges the layers, meaning that when placed in an appropriate polar solvent (Methods) the

175 anionic PNRs can dissolve; agitation (sonication or stirring) can encourage the individual

176 ribbons to fully separate. This mechanism explains the remarkable width uniformity, the

177 exclusive zigzag alignment, the smooth (fragment free) surfaces, and the prevalence of

178 monolayer PNRs (alternative liquid exfoliation strategies for BP, i.e. routes without

179 intercalation, typically result in predominantly greater thickness sheets[7]).

180

181 The collective optical properties of PNRs deposited on graphite were investigated with

182 Raman and Photoluminescence (PL) spectroscopies (Methods). All Raman spectra (example

183 Fig. 3g) exhibit peak positions, widths and relative intensities (Extended Data Fig. 9)

184 consistent with mechanically exfoliated few layer phosphorene, though with additional peaks

185 (Fig. 3g inset) attributable to the expected symmetry-breaking at the ribbon edges[30]. The

186 PNRs luminesce emitting at ~1.4 eV (Extended Data Fig. 9, Methods) consistent with

187 predictions that single layer PNRs are semiconductors with optical gaps in this energy

188 range[14]. Core-loss electron energy loss spectroscopy (EELS) at the P $L_{2,3}$ edge from an

189 individual PNR (Extended Data Fig. 3) demonstrates that the P environment is similar to

190 measurements and calculations of pristine BP showing no oxidation[31]; low-loss EELS

191 (Extended Data Fig. 3) resolves the expected plasmon peak at ~19 eV, as measured in bulk

192 BP and few layer phosphorene[31]. Notably, these features are sensitive to oxidation and defect

193 concentration[31] and thus further confirm the structural integrity of the PNRs. However,

194 though stable in an inert atmosphere (in solution and once deposited on a substrate), a multi-

195 technique stability study (Methods, Extended Data Fig. 10) reveals that deposited PNRs

196 gradually oxidise upon air exposure, similar to 2D phosphorene[6].

197

8

198 The PNRs produced have a remarkable range of widths, aspect ratios and lengths when

199 compared with nanoribbons of other materials, while crucially maintaining high width

200 uniformity. Significantly, the production method is scalable, and the stable liquid dispersions

201 permit the PNRs to be efficiently manipulated into thin films, membranes, composites,

202 electrodes, heterostructures and devices[7,29]. Zigzag PNRs have been predicted to exhibit a

203 variety of novel effects[14,17-19,21] and this alignment means that the fast transport of ions is

204 along the ribbon axis, important for battery applications[8,24]. For (opto)electronic devices

205 PNRs are predicted to offer band-gaps ranges distinct from other 2D materials and high hole

206 mobilities[20,25]. For these applications bifurcations present unique possibilities for fabricating

207 seamless transitions for integrated electronics.

208

209 **References**

210

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291 declare no competing financial interests. Readers are welcome to comment on the online

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293

294 **Author Contributions** M.C.W. discovered the PNR production method and produced the

295 samples. M.C.W. developed the production method with input from P.L.C., N.T.S. and

296 C.A.H. The HS-AFM measurements were performed and analysed by L.P., O.D.P., F.R-P.

297 and M.C.W. L.P. wrote the automated HS-AFM ribbon detection and step height

298 measurement algorithms. F.R-P. wrote the automated ribbon width measurement algorithm

299 and produced the HS-AFM movie. M.C.W. and V.T. performed and analysed the TEM.

300 T.S.M., M.C.W. and C.A.H. performed the electroplating, T.S.M. collected and analysed the

301 XPS data, C.A.H. collected and analysed the Raman and PL data with input from S.P.B.

302 P.L.C measured the UV/vis absorption spectra. M.C.W. and C.A.H. planned the experiments

303 and wrote the paper with input from all the authors. C.A.H. directed the project.

304

305 **Fig. 1 | TEM characterisation of PNRs**. **a**, The crystal structure of black phosphorus. **b**,
306 TEM micrograph (scale bar 10 µm) of PNRs drop-cast from liquid dispersion shown in inset.
307 **c**, (left) Scatter plot of PNR length as a function of width taken from 940 PNRs measured
308 using TEM, (right) histograms of the associated aspect ratio (top), and the widths (middle)
309 and lengths (bottom) corresponding to the dashed rectangle on the scatter plot. **d**, composite
310 TEM micrograph of an ~11 µm PNR on a continuous carbon TEM grid that has folded upon
311 drying, red arrows indicate the zigzag crystallographic direction determined from SAED
312 (Methods) (scale bar 1 µm), dashed boxes demarcate the different images from which the
313 composite is produced. **e**, SAED pattern corresponding to the blue box in **d** (scale bar 5 nm^{-}
314 ^{1}). **f**, Micrographs of PNRs, deposited on holey carbon TEM grids, displaying extreme
315 flexibility: (left) composite TEM micrograph of a twisted ribbon with radius of curvature 5.5
316 ± 0.5 nm at the region marked by blue arrows and (right) High Angle Annular Dark Field
317 (HAADF) image of a PNR (scale bar, both 500 nm). **g** High Resolution TEM (HRTEM)
318 micrograph of a folded PNR, outlined by yellow dashes for visibility (scale bar 500 nm); a
319 high magnification image through bend (top right), corresponding to the dashed box and
320 showing seven distinct BP layers (scale bar 2 nm), and line cut perpendicular to the layers
321 showing the two P atom planes in BP indicated by red and blue lines. **h**, HRTEM micrograph
322 through the dashed box from the flat region of the ribbon in **g**, showing the ordered atomic
323 lattice with associated FFT (bottom right) and zoom (top right) (scale bars 10 nm, inset 1 nm,
324 FFT 10 nm^{-1}) peaks in the FFT are indexed in Extended Data Fig. 3.

325

326 **Fig. 2 | AFM characterisation of PNRs. a**, HS-AFM images of 1.5 µm-long sections of
327 PNRs with heights corresponding to 1-5 phosphorene layers, in 3D view (top) and the same
328 dataset (bottom) rotated with the view direction through the ribbon length (scale bar 500 nm).
329 **b**, Histogram of the PNR layer number for 230 ribbons deposited within a 300 x 300 µm area
330 of substrate. **c**, Histogram of the widths of the PNR shown in **d** measured at 2,300 points
331 along its length (error bars) and Gaussian fit to this data (solid line). **d**, HS-AFM micrograph
332 of a monolayer PNR (scale bar 500 nm) **e**, Large area, composite HS-AFM micrograph of a
333 >75 µm long PNR (scale bar 10 µm), plotted alongside gradient image (Methods) for clarity.
334 Zoomed sections corresponding to the dashed boxes on the central image are also shown
335 demonstrating: bifurcations (top left) and a junction of two PNRs crossing (bottom right)
336 (scale bars both 500 nm).

337

338 **Fig. 3 | PNR formation (a-f) and Raman spectroscopy (g) of deposited PNRs. a-c**, TEM
339 images showing the process of ribbon formation: **a**, Li-BP crystal exhibiting unidirectional
340 cracks (scale bar 250 nm); **b**, Li-BP demonstrating in plane splitting as ribbons are formed

341 (scale bar 250 nm), the full image is presented in Extended Data Fig. 8; **c**, composite
342 micrograph of individualised PNRs following bath sonication (scale bar 1 μm). **d**, Schematic
343 of the electrodeposition setup; patterned Pt on Si/SiO$_2$ as working (positive) and counter
344 electrodes and a Pt wire quasi-reference electrode (offset in the direction of the page). The
345 optical image shows the grid over which Raman mapping was performed following
346 deposition, the lighter coloured region is the Pt coating on the green Si/SiO$_2$. **e, f** the intensity
347 of the fitted phosphorene A$_g^2$ and silicon peaks (scale bars 20 μm) on the electrode following
348 plating. **g**, example Raman spectrum from PNRs drop-cast onto graphite (Methods).

349

350

351

Methods

Production of phosphorene nanoribbons

354 <u>1. Intercalation of BP crystals</u> Macroscopic BP crystals (Smart Elements, 99.998% purity)

355 were first outgassed at 100 °C under dynamic vacuum (< 10^{-6} mbar) for one week. Without

356 exposure to air, the outgassed crystals were loaded along with lithium metal (99.9% Sigma

357 Aldrich) at a stoichiometric ratio of Li:8P, in a quartz reaction tube and attached via a glass-

358 metal transition to a leak-tight, custom, gas-handling manifold. The tube was immersed in a

359 propan-2-ol bath and the temperature cooled to, then maintained at, -50 °C using a Julabo

360 FT902 chiller. High-purity ammonia gas (Sigma Aldrich > 99.99%) was then condensed onto

361 the BP and Li, dissolving the alkali metal. The BP was left submerged in the dilute lithium-

362 ammonia solution (concentration < 1 mole percent metal) for 24 hours, during which time

363 intercalation occurred. Following this process the ammonia was slowly removed by cryo-

364 pumping, and the intercalated BP crystal was then further dried by vacuum treatment (< 10^{-5}

365 mbar for 1 hour), before being removed to a high purity argon glovebox (O$_2$, H$_2$O < 0.1

366 ppm).

367

368 <u>Choice of alkali metal to BP ratio</u> Attempts to intercalate BP with alkali metals are known to

369 result in a mixture of products including un-intercalated BP, intercalated BP and alkali metal

370 phosphides[8,26-28,32-38]. Recently a careful experimental study of the relative concentrations of

371 these reaction products, depending on the stoichiometric ratio of metal added to the BP

372 (M:P), was reported[26]. This work, in which BP was intercalated via exposure to a sodium or

373 potassium melt in an inert atmosphere, demonstrated that intercalation is always

374 accompanied by some degree of phosphide formation, the relative concentration of which

375 increases with increasing M:P ratio. Furthermore, successful intercalation of BP only

376 manifests as a subtle change in the associated X-ray diffraction (XRD) pattern. Another

377 recent BP intercalation study, using the same ammonia-based intercalation method employed

378 here, again found no well-defined layer increases typical for intercalation compounds[39]. We

379 also found that increasing the M:P ratio concomitantly increases the proportion of phosphides

380 produced. If a stoichiometry of M:4P was used, PNRs were produced (following solvent

381 addition) but alongside a large amount of debris/phosphides. However, decreasing the

382 stoichiometry to M:16P significantly lowered the eventual yield of PNRs. A compromise of

383 M:8P was therefore chosen, which produced a similar eventual ribbon yield to higher metal

384 ratios while significantly reducing the phosphide/debris production. Sodium (99.95% Sigma

385 Aldrich) intercalation, i.e. instead of using lithium, was also found to be effective at

386 producing PNRs.

387

388 <u>Characterisation of Li intercalated BP</u> The lithium-intercalated BP (Li:P ratio 1:8) was

389 investigated by Raman mapping experiments (experimental details below), the results are

390 presented in Extended Data Fig. 8. Upon lithium intercalation, a number of new Raman peaks

391 appear Extended Data Fig. 8a, b (top panels) similar to those reported for Na- and K-

392 intercalated BP[26]. Also for the intercalated sample, there is a significant down shift of the A_g^2

393 peak position from 467 cm^{-1} in pristine BP[40,41] to 462 cm^{-1} (mean) in the intercalated crystal

394 (Extended Data Fig. 8d) though with a broad spread of values (standard deviation 0.6 cm^{-1})

395   indicating the doping is inhomogeneous. A similar downshift was previously observed for Na

396   and K intercalation upon doping[26]. Extended Data Fig. 8f is a map scan of the A_g^2 position

397   for spectra taken in the red rectangle of the bottom panel in Extended Data Fig. 8c. The

398   position of the A_g^2 peak (indicating the extent of doping) is found to vary in stripes aligned in

399   the same direction as the unidirectional features seen in the optical micrographs of Extended

400   Data Fig. 8c. Raman mapping was performed in two sample orientations, with the stripes

401   parallel and perpendicular to the incident laser polarisation. The orientation had a significant

402   effect on the A_g^1/A_g^2 peak intensity ratio (Extended Data Fig. 8e) with the ratio being notably

403   larger with the laser polarisation parallel with the stripes (~0.8 compared with ~0.2). The

404   Raman spectra from pure BP are known to have a strong polarisation dependence, although it

405   should be noted that the dependence is different for different sample thicknesses and laser

406   wavelengths [40-43]. In particular, spectra of bulk BP indicate a A_g^1/A_g^2 intensity ratio

407   maximum for polarisation in the zigzag and minimum in the armchair direction[42,43].

408   Therefore, the peak intensity changes observed here imply that the doping stripes are parallel

409   to the zigzag direction. This inhomogeneous and directional doping is consistent with the

410   proposed mechanism and with in-situ experiments in Ref [27].

411

412   Finally, the Li-intercalated crystal was exposed to air and the measurements repeated

413   (Extended Data Fig. 8a, b bottom panels) following similar experiments in Ref [26]. The

414   Raman spectra show disappearance of the intercalation peaks so that only peaks of pure BP

415   remain, with the A_g^2 peak reverting to 466.8 cm^{-1} (standard deviation 0.1 cm^{-1}), (Extended

416   Data Fig. 8d). This data indicates that during air exposure the crystal de-intercalates.

417

418   A HS-AFM micrograph of the surface of the Li-BP crystal is presented in Extended Data Fig.

419   8h. The crystal surface shows a ribbon that is liberated from the surface of the crystal with a

420   corresponding 'trench' left behind, indicating that ribbon formation occurs during

421   intercalation (Extended Data Fig. 1 step 5).

422

423   The colour change throughout the intercalation process is noteworthy. For most layered

424   materials, during ion intercalation via the ammonia route, the originally deep blue solution

425   (colour arising from the solvated electron) eventually turns colourless (pure ammonia) with

426   the intercalated layered material left at the bottom of the container[29]. In the current work, an

427   orange solution was always found above the intercalated crystal, presumably owing to the

428   presence of phosphides, which are soluble in ammonia as previously reported[37,38]. The

429   solubility of the phosphides in ammonia is beneficial since it allows the amount of this

430   undesirable by-product to be decreased following intercalation.

431

432   <u>2. Formation of PNR dispersions</u> Within a high purity argon glovebox an anhydrous aprotic

433   solvent (typically 1 mL) was added to the intercalated Li-BP crystal (typically 1 mg) in a

434   glass vial. The vial was then sealed and placed in an ultrasonic bath (Ultrawave QS3, 50 W)

435   for 1 hour; the bath water was changed every 20 minutes in order to keep the water

436   temperature below 40 °C. Alternatively, stirring the Li-BP/solvent mixture using a glass

437   coated magnetic stir bead for 1 week inside the glovebox was found to be equally effective,

438   and produced PNRs that were indistinguishable (via TEM analysis) from those produced via

439   1 hr bath sonication. To remove larger stirred-up fragments of Li-BP crystals, low-g

440   centrifugation was used at 385 g (2000 RPM) for 20 minutes (Hettich EBA 20). For the

441   spontaneously dissolved sample (Extended Data Fig. 6), solvent was added carefully to Li-

442   BP, so as not to disturb the powder and left for one week, before an aliquot was removed

443   from the uppermost portion of the solution for analysis. A schematic representation of the

444   PNR production process is shown in Extended Data Fig. 1.

445

446   The solvents that successfully produced stable dispersions of high-quality PNRs were all

447   polar and aprotic, similar to those used to dissolve other charged nanomaterials, that is,

448   chosen not to react with the charged nanomaterials but to permit thermodynamic

449   dissolution[29,44,45]. Of the polar, aprotic solvents tested, n-methyl-2-pyrrolidone (NMP),

450   dimethylacetamide (DMAc), dimethylformamide (DMF) and acetonitrile, produced ribbons,

451   tetrahydrofuran (THF) and dichloromethane (DCM) did not. Of the effective solvents,

452   DMAc, DMF and acetonitrile produced more concentrated ribbon dispersions (from TEM

453   inspection), however, NMP dispersions contained a lower percentage of non-ribbon BP

454   fragments and was therefore the solvent adopted during this work.

455

456   Attempts at PNR production were also made using the following solvents: IPA, acetone,

457   water and hexane. These solvents were all ineffectual at producing ribbons. Hexane produced

458   no dispersed material. IPA, acetone and water resulted in a mixture of short amorphous

459   species and qualitatively shorter ribbons however, little crystallinity was evident from SAED,

460   suggesting significant functionalisation or chemical reaction of the ribbons or the intercalated

461   crystal.

462

463   <u>Control experiments</u> The procedure described above for forming PNRs was repeated for both

464   BP crystals that had not been intercalated and BP crystals that had just been submerged in

465   liquid ammonia (but with no metal present). In both cases, neither ribbon-like fragments nor

466   any exfoliated (sheet-like) BP were found in TEM.

467

468   **Deposition of PNRs onto substrates**

469   PNRs were drop-cast from solution in NMP onto freshly cleaved graphite (HOPG, GE

470   Advanced Ceramics ZYH grade) or TEM grids (details below). NMP, though commonly

471   used in processing of nanomaterials[46], is a high boiling solvent with low vapour pressure that

472   can also polymerise at high temperatures[47], so its removal can be problematic. Therefore

473   (unless stated differently) the following drying procedure was adopted to remove NMP from

474   drop-cast substrates. The NMP solution was dropped onto the substrate in a high purity Ar

475   glovebox (O_2 & H_2O <0.1 ppm) using a micro-pipette. The substrate was then transferred

476   (air-free) to a custom-built apparatus and subjected to Ar gas (BOC pureshield argon) flow

477   for ~8 hours at room temperature. Without exposure to air, the substrates were then

478   evacuated to 10^{-6} mbar using a turbomolecular pump and left under dynamic vacuum

479   (continuous pumping) for one week before the temperature was increased to 100 °C for a

480   further week. The samples were then removed without exposure to air and stored in a high

481   purity argon glovebox. Thus (unless stated otherwise) all deposited samples PNR samples

482   investigated were kept in inert conditions for at least two weeks prior to experiment.

483

484   The drop-coated PNRs are not expected to be doped or intercalated with lithium ions for the

485   following reasons: 1. All Raman spectra for Li-BP show strong downshift of the A_g^2 peak

486   and extra peaks (Extended Data Fig. 8a, b), which are absent from all spectra taken on

487   deposited PNRs for which A_g^2 is in its undoped position (Extended Data Fig. 9d); 2. The

488   heights of the multilayer (1-5 layers) PNRs (Extended Data Fig. 4) closely match the layer

489   heights expected for unintercalated BP, whereas intercalated ions are known via calculations

490   and experiments to increase the out-of-plane lattice parameter by up to 20% (Refs 26,27); 3.

491   Doped/intercalated BP is metallic[26,39] and therefore would not be expected to luminesce

492   (Extended Data Fig. 9f). Strategies exist for removing residual alkali metals from SWCNT

493   and graphene deposited from analogous solutions of their charged species[48].

494

495   XPS data taken over large areas (spot diameter 400 μm) of deposited PNRs on graphite

496   (Extended Data Fig. 10h) could not detect the presence of any residual phosphides (within the

497   limits of the measurement) which would appear as a peak at lower binding energies (~129

498   eV) Ref [49].

499

500   Electrodeposition was performed using a custom-built three-electrode cell inside a high

501   purity glovebox for 24 hours using a Gamry Interface 1000 potentiostat. A platinum wire was

502   utilised as a quasi-reference electrode and the counter and working (positive) electrodes were

503   formed of oxidised silicon wafers that were partially coated with Pt (PI-Kem). The deposition

504   was undertaken at a static potential of 1.1 V, which was held for 24 hours. For electroplating

505   we used DMAc as a solvent to minimise solvent decomposition products.

506

507   **Stability of PNRs in solution and in air**

508   To investigate the stability of the PNRs in solution, we monitored the UV/Vis absorption

509   spectrum of the solution over 50 days similar to studies in Refs [50,51]. The UV/Vis

510   absorption spectrum of PNRs in NMP (Extended Data Fig. 9g) is qualitatively very similar to

511   that of liquid dispersions of BP nanosheets[50], i.e. showing increased absorbance at lower

512   wavelengths and small features below 500 nm (Refs 50,52). The relative change in

513   absorbance at 465 nm over 50 days was fitted with an exponential decay function following

514   the analysis outlined in Refs [50,51] (Extended Data Fig. 10i). In these references, the

515   decrease in absorbance over time is attributed to the dispersed BP nanosheets gradually

516   degrading into reaction products that do not absorb in this spectral region[50]. Therefore, from

517   the empirical fit, the decay constant and the unreacted fraction of pristine BP that remains can

518   be extracted. For our charged PNRs in NMP, measured in inert conditions, we find a

519   significantly greater unreacted fraction (98.5 ± 0.4 %) than the equivalent optimal case for

520   BP nanosheets dispersed in deoxygenated CHP in inert atmosphere. Moreover while the

521   researchers in Ref [50] shake samples before each measurement to 'avoid sedimentation

522   effects', in contrast, we took care not to disturb our PNR solutions between measurements, in

523   order to establish whether or not sedimentation occurs. The comparatively small decrease in

524   absorbance therefore also demonstrates that the PNR dispersions are stable against

525   flocculation. This stability is expected since the PNRs spontaneously dissolve (Extended

526   Data Fig. 6) because they are charged[29,44,45]. Reaction with residual water/oxygen in the

527   solvent could account for the small decrease in absorbance observed over the 50 days.

528

529   Though PNRs were found to be stable in inert conditions, BP is well-known to be air-

530   sensitive with an increasing instability to oxidation as the number of layers are reduced,

531   though the exact details of the mechanism are currently under debate[43,53-56]. We therefore

532   studied the effect of increasing air exposure on PNRs deposited onto HOPG substrates drop-

533   cast from the same solution using XPS, Raman spectroscopy and HS-AFM. The relative

534   humidity was monitored to be ca. 50% over the course of the experiment.

535

536   Following air exposure AFM measurements on BP typically reveal a marked increase in

537   surface roughness due to water adsorption[43,53,54]. This process causes rapid further

538   degradation and fragmentation of the BP crystal[43,53,54]. We used HS-AFM to monitor changes

539   in height and width of the same 1 and 2 layer PNRs over 6 days Extended data Fig. 10a-f. In

540   contrast to 2D BP studied in air[43,53,54] we measured no significant change in height over the 6

541   days. However, we did measure a narrowing of the ribbons' width, discernible after 6 days in

542   air for both 1 and 2 layer PNR, (Extended Data Fig. 10a-f, method detailed below). The edge

543   erosion for the PNRs exposed on a surface is similar to that recently measured (and

544   previously predicted[50]) for few layer BP if it is fully submerged in water in order to stop

545   droplet build up on the surface[55].

546

547   Raman studies of BP have consistently noted a decrease in A_g^1/A_g^2 integrated intensity ratio

548   with increasing air exposure, which has been demonstrated to be a metric for monitoring

549   degradation on mechanically exfoliated phosphorene[43,53]. We therefore performed Raman

550   mapping measurements on PNRs deposited on HOPG substrates over 6 days of air exposure

551   (experimental details below). The air free PNRs have an A_g^1/A_g^2 ratio of 0.27 ± 0.02,

552   (Extended Data Fig. 9e) consistent with single/few layer BP[40,43,53]. However, unlike 2D

553   phosphorene, with increasing air exposure, the average value of the A_g^1/A_g^2 integrated

554   intensity ratio does not change as a function of time (Extended Data Fig. 10g). On the other

555   hand, the A_g^2 peak:background ratio decreases monotonically (Extended Data Fig. 10g)

556   indicating the degradation of the PNRs[53]. We also found a gradual decrease in average width

557   and energy of the A_g^2 peak over the 6 days (Extended Data Fig. 10g). This trend could be

558   explained by the monolayer PNRs degrading at a faster rate than the multilayer PNRs since

559   for 2D BP the A_g^2 mode is known to both narrow and soften with increasing number of

560   layers[53].

561

562   XPS data of fresh and air exposed PNRs are plotted in Extended Data Fig. 10h. Similar to

563   both bulk BP[57] and 2D few layer BP[58], the PO_X contribution (broad peak at ~134 eV)

564   increases gradually over time. Though it should be noted that few/monolayer phosphorene is

565   less air-stable than multilayer/bulk BP[54]. Eventually after 6 days the P-P contribution at ~130

566   eV becomes unmeasurable. The POx contribution for the 'fresh' PNRs (2 – 5 minute air

567   exposed during transfer to the spectrometer) is 15% of the total area, which the same as that

568   reported for few layer phosphorene sheets created through liquid exfoliation methods[50]. Here

569 the surface sensitivity of XPS should be highlighted, as while the PNRs that are isolated or at

570 the surface of collections of PNR oxidise, multilayer PNRs or those buried underneath are

571 protected, evident from the Raman response even after 6 days.

572

573 Overall, the data show that PNRs are similarly susceptible to oxidation as few layer BP but

574 the accelerated decomposition following water adsorption is significantly less pronounced,

575 which perhaps explains a much slower fall off of the A_g^1/ A_g^2 intensity ratio with air

576 exposure. Here, it should be noted that there are many methods that have been devised

577 specifically to protect BP flakes from air during processing, as summarised recently[54]

578 typically by liquid[43,50] or solid capping[54] that could be used to protect PNRs during

579 processing.

580

581 **Electron microscopy**

582 TEM samples were made by drop casting ribbons from dispersion onto holey/continuous

583 carbon 200 or 300 mesh Cu or Au TEM grids (EM Resolutions). TEM was performed on a

584 Jeol JEM 2100 equipped with a LaB_6 source operated at 200 kV. During transfer to the TEM

585 chamber, the grids were exposed to air for approximately 2 minutes for mounting in the

586 holder and ~5 minutes for evacuating the holder before insertion in the microscope.

587 Specifically for EELS spectroscopy (Extended Data Fig. 3l, m) PNRs were drop-cast inside

588 an Ar atmosphere glovebox on C-flat TEM grids that were heated to 80 ºC for solvent

589 evaporation. They were then transferred to the TEM as noted above with minimum exposure

590 to air. The electron microscopy was performed on a double spherical aberration corrected

591 ThermoFisher Scientific™ Titan Themis 60-300 operated at 60 kV. Electron energy-loss

592 spectroscopy (EELS) was performed with a Gatan GIF Quantum™ spectrometer using the

593 Gatan ADF STEM detector. The monochromator was excited and a 0.3 eV energy resolution

594   was achieved. All spectrum images (SI) were collected using Gatan DigitalMicrograph™

595   with a camera length at 29.5, giving a beam convergence semiangle of 26 mrad, a collection

596   semiangle of 19.8 mrad, and an ADF inner detection angle of 41.2 mrad. Spectrum imaging

597   was performed in dual EELS mode and data were acquired at 0.1 eV/channel dispersion.

598   Typically, spectra were collected from areas of 200 x 50 nm^2 that were at the edges of the

599   carbon support in order to avoid interfering signal from the carbon substrate. Still, signal

600   from the low-loss, broad peak at 5 eV stemming from amorphous carbon was visible in the

601   spectra. Finally, it is noted that core-loss probing of the oxygen K edge showed no oxidation

602   of the sample.

603

604   To assess the distribution of ribbons within a sample, the TEM grids were randomly sampled

605   over each quarter of a TEM grid. Around each randomly selected position, an area of 56 μm^2

606   (7.5 μm x 7.5 μm) was explored since multiple frames were required to image individual

607   PNRs with sufficient resolution to measure their width along their length. Ribbon dimensions

608   were measured using Gatan Digital Micrograph software. As can be seen from TEM figures

609   from continuous carbon grids (Fig 1b, Fig 1d) as well as PNRs, the grids show there are an

610   amount of small debris, most likely phosphides or small fragments of BP that have been

611   produced during intercalation or sonication.

612

613   It is noted that degradation of the ribbons after electron beam exposure occurred in both 60

614   kV and 200 kV after several minutes. The electron dose rates, primarily responsible for the

615   amorphisation of the ribbons, were kept low to preserve the integrity and crystallinity of the

616   ribbons during data acquisition.

617

618   Composite TEM micrographs (Figs. 1, 3, and Extended Data Fig. 2 and 3) were constructed

619   by superposing two or more overlapping images and are demarcated by dashed lines.

620

621   The crystallographic orientation of the ribbons was determined by indexing SAED patterns.

622   Indexing was performed using Gatan GMS 3 software by comparing measured spot distances

623   to the simulated TEM diffraction pattern from the crystal structure of BP. The orientation of

624   this pattern reveals the real-space orientation of crystal planes and therefore the

625   crystallographic alignment.

626

627   **High-Speed Atomic Force Microscopy (HS-AFM)**

628   Large area, high-resolution topography maps were generated using a contact-mode HS-AFM

629   (Bristol Nano Dynamics Ltd, UK) as used in previous studies on solution deposited

630   nanomaterials[29,59,60,61]. This instrument permits the rapid acquisition of data across areas

631   thousands of square microns in size with sub-nanometre height resolution. The typical image

632   size used in this work was 2 x 2 µm, corresponding to a pixel size of 2 x 2 nm, and data were

633   collected at a rate of 2 frames per second. Contact-mode silicon nitride cantilevers (Bruker

634   MSNL, tip radius 2 nm nominal, 12 nm max) were used throughout.

635

636   HS-AFM samples were prepared by drop casting onto freshly cleaved graphite (HOPG)

637   substrates. The substrate consists of large flat regions bounded by graphite step edges ranging

638   from a single atomic layer to many tens or hundreds of layers high. To ensure that HOPG

639   step edges were not miscategorised as PNRs, a user-guided analysis routine was

640   implemented. First, the position and orientation of any PNRs within the candidate HS-AFM

641   frame were identified, after which the analysis of their height and width was passed to an

642   automated algorithm. Using custom software written in LabVIEW (National Instruments),

643 identified PNRs were highlighted by drawing a rotated rectangular region of interest. The

644 region of interest was then extracted from the raw HS-AFM data using a local thresholding

645 routine in order to identify the PNR against the HOPG background and produce a binary

646 mask of the ribbon (1) and the HOPG background (0). This binary mask was then duplicated,

647 with one copy being dilated (expanded) with two iterations of a 3 x 3 structuring element (to

648 include the edges where the PNR touches the HOPG) and the other eroded (reduced) by two

649 iterations (to exclude these same edges). These erosion and dilation steps ensure that the two

650 masks exclude the transition region between the HOPG and the top of the PNR and prevent

651 the inclusion of edge pixels where accurate categorisation as either an HOPG or PNR pixel is

652 difficult. The resultant binary masks were then used to isolate the HOPG background and the

653 top of the PNR respectively. Once isolated, the median of the HOPG background and PNR

654 pixel heights were calculated and the difference used to classify the layer thickness for each

655 pixel in the ribbon mask. The mean height of the background for all measurements was set to

656 zero. For determination of the heights and roughnesses of 1-5 layer PNR, as presented in

657 Extended Data Fig. 4, the number of individual pixel-height measurements (taken over

658 multiple locations, PNRs and substrates) are: HOPG substrate (886,908 measurements); and

659 for PNRs of 1 layer (61,181 measurements), 2 layer (50,637), 3 layer (18,740), 4 layer

660 (78,514) and 5 layer (28,816). Though such step height measurements are highly sensitive to

661 uncertainty (noise) this uncertainty is random, not systematic. As such it broadens the

662 Gaussian distribution of step heights measured but does not affect the mean of the

663 distribution. The result is an average height of the PNRs independent of signal-to-noise

664 absolute values, provided a suitably large number of measurements are performed. In each

665 case the extracted roughnesses, σ, are given by the standard deviation from the Gaussian fit to

666 the associated height histograms, following the methods described in Lui *et al.*[62].

667

668   This same software was used to track the edges of the PNRs and measure their widths along

669   their lengths (Fig. 2c, d). The neutral or central axis of each PNR was calculated by fitting a

670   cubic spline to both tracked edges and then calculating the mean path from these two fits. The

671   distance from each edge to the neutral axis was then determined. This facilitates the

672   calculation of a bulk mean width and standard deviation but does not evaluate the line edge

673   roughness (LER) or line width roughness (LWR)[59,63].

674

675   For the 75 μm single PNR (Fig. 2e), the data was taken while manually tracking the PNR in

676   real time. To create the composite image overlapping frames were offset by the difference in

677   the median pixel value in their respective regions of overlap. Then, the newer frame was used

678   to overwrite the data in the overlap region. Due to the high signal-to-noise ratio, there was no

679   need to perform any image averaging. In this way, a consistent signal-to-noise was preserved

680   regardless of the number of frames overlapping a given area. The XY position of each frame

681   was recorded with nm resolution by the long-range positioners (SmarAct, Germany) used to

682   pan the HS-AFM image window across the sample surface. This information was used to

683   arrange the HS-AFM frames into their approximate locations. Final adjustments to the offsets

684   between frames were carried out manually to account for drift of the sample relative to the

685   positioners. The very high aspect ratio of this PNR meant that the typical methods used to

686   present AFM data were unsuitable. Since the PNR traverses many HOPG steps tens of nm in

687   height (but is itself less than 3 nm high for much of its length) it required a large dynamic

688   range to visualise properly. To supplement the composite height map of this PNR and

689   improve readability, a gradient image of the same region was calculated. The gradient image

690   accentuates the surface texture by reducing the dynamic range of the image, aiding the

691   display of nanoscale features present on large background slopes in the same way as the

692   error/deflection image generated during conventional contact-mode AFM. The gradient

693   image was calculated from the composite height map along the fast scan direction using a

694   five pixel moving window. The magnitude of the gradient was selected for display in Fig. 2e

695   to give the PNR greatest contrast against the HOPG steps and background.

696

697   To analyse the distribution of PNR layer thicknesses (Fig. 2b), the HS-AFM was set to

698   automatically image a 300 x 300 μm region in the centre of an HOPG surface. A raster scan

699   translated the HS-AFM image window across the full 300 x 300 μm area and the resultant

700   dataset was analysed using the same user-guided routine as described above.

701

702   For the air stability study, PNRs from the same location Extended Data Fig. 5e, f were

703   measured over a six-day period (Extended Data Fig. 10a, d). Measurements were performed

704   as detailed above, however an additional calibration step was included to determine the shape

705   of the imaging tip of the AFM cantilever before each scan. This was performed to ensure that

706   any observed changes in the height or width of the PNRs could be correctly attributed to real

707   variations in the ribbons, rather than arising from tip convolution effects[64], which may change

708   over the different days. To achieve this, a HOPG trench on the same sample was imaged, this

709   trench is expected to remain stable throughout all measurements as HOPG is not sensitive to

710   atmospheric conditions. As such, any variation in the measured width of the trench can be

711   attributed to fluctuations in the shape of the imaging tip arising from picking up contaminants

712   from the sample surface during scanning, or wear of the tip itself. The HOPG trench was

713   therefore used to correct for the effects of tip sharpness variance.

714

715   **Optical characterisation.**

716 Raman and PL spectra were collected using a Renishaw In-Via microscope equipped with a

717 488 nm laser through an x20 objective. For the Raman spectra of plated and drop-cast PNRs,

718 Li-BP and the PL experiments, the samples were contained in argon environment in a custom

719 made glass cell. For the air-free Raman measurements (Fig 3, Extended Data Fig. 9), air

720 exposure (Extended Data Fig. 10) and PL measurements samples were dropped onto freshly

721 cleaved HOPG from the same solution and the maps taken over high local concentrations of

722 PNRs to measure their collective optical properties. For the air-free Raman spectra, 351

723 spectra from a 15 μm x 25 μm grid were fitted with 3 Lorentzian functions between 350 and

724 500 cm^{-1}, using a custom implementation of the Levenberg-Marquardt algorithm and the

725 positions, intensity and widths extracted. These data were then used to create histograms of

726 the positions and widths and the relative intensities across the map, from which Gaussian fits

727 (Extended Data Fig. 9) were used to extract average positions and standard deviation of these

728 distributions. For the air exposure experiments the same area was probed, though on a less

729 dense grid of between 90-100 spots and with shorter counting times in order keep each

730 overall map acquisition to below 2 hours. For the plating measurements the map scan of the

731 positive electrode (Fig. 3c) - spectra from 255 points on an 80 μm x 70 μm grid were

732 measured, and each was fitted with Lorentzian line-shapes in the window for the BP peak at

733 467 cm^{-1} and silicon peak at 520 cm^{-1}. Equivalent data were taken from the counter electrode

734 and showed no preferential PNR deposition. For the Li-BP crystal measurements, the four

735 maps were taken over the same region of the crystal surface with the polarisation of the

736 incident laser perpendicular or parallel to the vertical features in the optical image. Spectra

737 from the Li-BP crystal were fitted with 8 Lorentzian functions as shown in Extended Data

738 Fig. 8a, b. PL spectra were recorded with a 1200 line/mm diffraction grating (as opposed to

739 2400 lines/mm for Raman spectra), using a long-pass filter (cut-on wavelength 700 nm) for

740   the low energy (< 1.74 eV) part of the spectrum to remove peaks originating from second

741   order diffraction on the grating.

742

743   Optical absorption spectra were measured on a Shimadzu UV-2600 spectrometer equipped

744   with an ISR2600Plus integrating sphere attachment in a 4 mm path length quartz cuvette. To

745   maintain an inert atmosphere the cuvettes were filled in the glovebox and sealed. A

746   background of pure solvent loaded in the same cell was subtracted from the spectra.

747

748   **XPS measurements**

749   XPS spectra were acquired using Thermo Scientific K-Alpha (mapping study) and Theta

750   Probe (oxidation study) spectrometers, both fitted with a monochromated Al K_α sources

751   (1486.6 eV). The P 2p spectra were fitted with mixed Gaussian/Lorentzian peaks (spin-orbit

752   ratio 1:2, 1/2: 3/2; peak separation 0.86 eV), a single Gaussian/Lorentzian was used to fit the

753   oxide peak due to the broader nature of oxide-derived spin-split core levels. XPS mapping

754   was performed over areas of ~5 mm^2 using a beam size of 400 µm^2 and step sizes of 400 µm.

755   The doublet of peaks at ~130.5 eV can be assigned to the P-P environment (P-O at ~134 eV)

756   (Ref 57) and the integrated area under this peak pair was used to construct the maps. For the

757   oxidation study, PNRs were dropped onto freshly cleaved HOPG in a low oxygen glovebox,

758   dried as described above, then exposed to atmosphere for increasing periods of time.

759

760   **Supplementary references**

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841

842   **Data availability** The datasets generated during and/or analysed during the current study are

843   available from the corresponding author on reasonable request.

844

845   **Extended Data Fig. 1 | Schematic of PNR production.** BP crystals were outgassed in a
846   quartz reaction tube (1) and lithium metal was added (2). The tube was cooled to -50 °C and

847 high-purity ammonia was condensed onto the BP and Li (3), dissolving the alkali metal to
848 form a Li:NH$_3$ solution. The BP was then left submerged in the Li:NH$_3$ solution for ~24
849 hours, allowing intercalation (4), before the ammonia was slowly removed. Without air
850 exposure, the intercalated BP crystal was transferred to a glovebox and placed into a vial (5)
851 and NMP was added (6). This vial was then placed in an ultrasonic bath for 1 hour and
852 centrifuged at low-g. This process resulted in solutions of PNRs (7).

853

854 **Extended Data Fig. 2 | Gallery of PNRs.** TEM micrographs showing PNRs (darker ribbon-
855 like features) deposited on 'holey-carbon' TEM grids (lighter webbed structure). **a**,
856 Heterogeneous PNRs of different widths. **b**, Micrographs of high aspect ratio (> 100) PNRs
857 with widths < 5 nm. Dashed boxes mark areas where a zoomed (and therefore higher
858 resolution) overlay has been superposed, solid boxes correspond to the extracted zoom insets.
859 To enhance visibility select PNRs have been outlined by dashed lines, otherwise, red arrows
860 indicate the location of the ribbon. **c**, Images of PNRs that demonstrate their flexibility.
861 Composite TEM images are demarcated by dashed, black boxes.

862

863 **Extended Data Fig. 3 | Electron microscopy, diffraction and spectroscopy of individual**
864 **PNRs. a-f,** SAED patterns (scale bar 10 nm^{-1}) taken at the locations corresponding to the
865 boxes marked in the composite TEM image in **g** (scale bar 1 μm). These images show the
866 zigzag crystallographic alignment along the length of the PNR, indicated by the red
867 arrows. **h**, indexed FFT transform (scalebar 10 nm^{-1}) of the HRTEM micrograph shown in
868 Fig 1h. **i**, STEM (scalebar 2.5 μm) and **j**, TEM (scalebar 2 μm) images of the same PNR for
869 which EEL spectra (**l,m**) were recorded. **k**, closer view (scale bar 1 μm) of PNR shown in **i**
870 (left), and spectrum image chosen at a suspended-in-vacuum part of the ribbon (right)
871 indicating as a red square the region from which EEL spectra shown in **l** & **m** were averaged.
872 **l**, Core-loss EELS at the P L$_{2,3}$ edge (130 eV) showing features in regions I, II and III that
873 correspond to features found in pristine few layer BP[31]. **m**, low-loss EELS spectrum showing
874 the expected plasmonic signature peak at ~19 eV and another feature at ~3.3 eV similar to
875 that found for few layer BP and attributed to surface plasmons[31]. The broad feature at ~5 eV
876 marked with an asterisk is from delocalized signal coming from the amorphous carbon
877 support.

878

879 **Extended Data Fig. 4 | Heights and roughnesses of 1-5 layer PNRs from statistical**
880 **analysis of HS-AFM images (Methods).** Normalised histograms (black error bars) and
881 Gaussian fits (solid blue line) of independent, automated, pixel-height measurements from
882 the HOPG substrate (far left curve) and for PNRs of 1 - 5 layers. The extracted average
883 heights (z) and roughness (σ) are shown above each ribbon. Scaled representations of the
884 crystal structures of 1-5 PNRs are overlaid.

885

886 **Extended Data Fig. 5 | HS-AFM of PNRs. a,** a zoom of the PNR from Fig. 2e (scale bar 5
887 μm). **b** zoomed image of the bifurcation found in **a** (scale bar 500 nm). **c**, **d** linecuts taken
888 from **b**, before (**c**) and after (**d**) the bifurcation, that demonstrate the ribbon self-cleaves from
889 its original height of ~3.5 nm (7 layers) to two branches of heights ~1.5 nm (3 layers) and ~2

890 nm (4 layers). **e**, **f**, HS-AFM images (scalebars 200 nm, 500 nm respectively) of areas over
891 which the stability study presented in Extended Data Fig. 10a-f was taken. In **e**, black box
892 corresponds to HOPG trench used to correct the stability data for tip effects (Methods) and
893 blue box corresponds to bilayer PNR in Extended Data Fig. 10d. In **f** the blue box
894 corresponds to the monolayer ribbon presented in Extended Data Fig. 10a.
895
896 **Extended Data Fig. 6 | Dimensions of spontaneously dissolved PNRs.** Length vs width
897 scatter plots of dispersed PNRs extracted from TEM data (Methods). The plot shows the
898 PNRs that have spontaneously dissolved from Li-BP crystals into NMP solvent (red circles)
899 as well as those formed via bath sonication (blue circles). The zoom (right) corresponds to
900 the dashed rectangle on the left-hand image and reveals that the spontaneously dissolved
901 PNRs are wider than those formed by sonication.
902
903 **Extended Data Fig. 7 | XPS and Raman spectroscopy of electrodeposited PNRs**. **a**, XPS
904 maps of the patterned-Pt positive (left), and negative (right) terminal electrodes from PNRs
905 electrodeposition. Maps were constructed from the integrated area under those P 2p peaks
906 assigned to the P-P environment (scale bar 500 µm). **b**, Schematic representations of the Pt
907 pattern (grey) on the positive (left) and negative (right) electrodes. **c**, an example P 2p
908 spectrum from, **a**, fitted with mixed Gaussian/Lorentzian peaks assigned to P-P bonding and
909 P-O surface contamination. **d**, patterned electrode showing grid over which Raman maps
910 presented in Fig. 3e, f were taken (scale bar 20 µm). The blue and red dots in **d** show the
911 specific locations where the example Raman spectra shown in **e**, were taken.
912
913 **Extended Data Fig. 8 | Characterisation of lithium intercalated-BP**. **a**, **b** Example Raman
914 spectra of Li-BP recorded with the incident laser polarisation perpendicular to (**a**) or parallel
915 (**b**) to the vertical features in **c** (bottom). The top two spectra of (**a**) and (**b**) are performed in
916 argon, the bottom two after 30 days in air from the same region in the sample. These spectra
917 are fitted (Methods) with a sum (red curve) of Lorentzian functions for BP (blue curves) and
918 intercalation (green curves) Raman modes. **c**, optical micrographs of a Li-BP crystal top
919 (scalebar 200 µm), and bottom zoomed in (scalebar 18 µm). The bottom image also shows
920 the area (dashed box) over which the Raman mapping data presented in **f** were taken from. **d**,
921 histograms of the positions of Li:P A_g^2 peak position in argon (orange) and after 30 days in
922 air (green). **e**, histograms of the A_g^1/A_g^2 peak intensity ratio for measurements performed
923 with the incident laser polarisation parallel (blue) or perpendicular (yellow) to the vertical
924 stripes in **c**. **f**, map of the position of the A_g^2 peak for data taken over the red box in **c**
925 (scalebar 5 µm). **g**, TEM image showing in-plane splitting of PNRs from a larger fragment
926 (scalebar 500 nm). **h**, HS-AFM image (top, scalebar 100 nm) and associated linescan
927 (bottom) of the surface of an Li-BP crystal showing a ribbon (line profile 1, black data)
928 liberated on the surface and the trench left behind (line profile 2, red data).
929
930 **Extended Data Fig. 9 | Collective optical properties of PNRs**. **a**, Example Raman spectrum
931 (black circles) taken from PNRs deposited on a graphite substrate in an argon atmosphere
932 (Methods). The spectrum is fitted with a sum (red curve) of three Lorentzian functions (blue
933 curves) corresponding to the A_g^1, B_{2g} and A_g^2 peaks of black phosphorus[40,41]. **b-d** histograms

934 of the positions (top) and widths (bottom) of the Raman modes and, **e**, the integrated
935 intensities ratios of the A_g^1:A_g^2 peak (top) and the B_{2g}:A_g^2 peak (bottom), extracted by fitting
936 351 independent spectra taken from the same sample of solution-deposited PNRs. From the
937 fits to the distributions in **b-d** the mean values and the standard deviations, given in brackets,
938 of the Raman peak positions and widths were determined to be: A_g^1 position 362.5 (0.2) cm^{-1},
939 width 3.3 (0.2) cm^{-1}; B_{2g} position 439.3 (0.2) cm^{-1}, width 5.4 (0.3) cm^{-1}; A_g^2 position 467.5
940 (0.2) cm^{-1}, width 3.7 (0.2) cm^{-1}. **f**, PL spectrum from PNR aggregates deposited on graphite,
941 peaks at high energy are Raman features from the PNR or the graphite substrate (the latter
942 marked by asterisks). Mechanically exfoliated single layer phosphorene emits at ~1.3 eV
943 (Ref 65). **g**, UV/Vis absorption spectra from a PNR solution (inset), the red circles mark the
944 positions of weak features below 500 nm.

945

946 **Extended Data Fig. 10 | Stability of PNRs**. **a**, HS-AFM images (scalebars 50 nm) of the
947 monolayer PNR shown in Extended Data Fig. 5f taken immediately (top) and following 6
948 days air exposure (bottom). **b**, histograms of the width (left) and height (right) of the PNR in
949 **a** taken immediately (blue) and after 6 days in air (yellow), each histogram has been fitted
950 with a Gaussian function (red). **c**, the width (left) and height (right) of the PNR over 6 days in
951 air taken from fits to histograms as shown in **b**. **d**, HS-AFM images (scalebars 50 nm) of the
952 bilayer PNR shown in in Extended Data Fig. 5e. **e-f**, the equivalent data as described in **b-c**
953 but taken for the bilayer ribbon in **d**. **g**, evolution of the Raman A_g^1:A_g^2 integrated intensity
954 ratio, the A_g^2:background intensity ratio, A_g^2 position and A_g^2 width (top to bottom
955 respectively) extracted by analysing maps of 90-100 independent spectra taken over the same
956 location from a sample of PNRs drop-cast onto graphite (Methods). **h**, evolution of XPS
957 spectra (data black dots, red curve fits to P peaks, blue curve fits to P-O peaks) taken from a
958 sample of PNR drop-cast onto graphite as a function of increasing air exposure (top to
959 bottom). **i**, Normalised absorbance at 465 nm (black dots) as a function of time taken from
960 the same solution of PNR in NMP (photograph shown in inset) over 50 days without
961 exposure to air. Red curve is an exponential function fit to the data (Methods).

962

a

Zigzag

[0b0]

Armchair

b

c

Ribbon length (nm)

Ribbon width (nm)

Frequency

Aspect ratio

Frequency

Ribbon width (nm)

Frequency

Ribbon length (μm)

d

e

(102)   (200)

(101)

h

l

f

g

Intensity

Distance (nm)

h

a

b

c

d

e

a

b

c

d

Pt

Si

e

A_g^2 Intensity

f

Si Intensity

g

B_{1g} B_{3g}^1

Raman shift (cm^{-1})

A_g^2

A_g^1

B_{2g}

Intensity (a.u.)

Raman shift (cm^{-1})