Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Production of Few-Layer Phosphorene by Liquid Exfoliation of Black Phosphorus

Jack R. Brent,[a] Nicky Savjani,[b] Edward A. Lewis,[a] Sarah J. Haigh,[a] David J. Lewis[a,b]* and Paul O'Brien[a,b]*

Corresponding Authors
Professor Paul O'Brien
Email: paul.o'brien@manchester.ac.uk.
Dr. David J. Lewis
Email: david.lewis-4@manchester.ac.uk

Tel: +44 161 275 4653.
Fax: +44 161 275 4616.

[a] *School of Materials, The University of Manchester, Oxford Road, M13 9PL, U.K.*
[b] *School of Chemistry, The University of Manchester, Oxford Road, M13 9PL, U.K.*

General

Black phosphorus was purchased from Smart Elements. *N*-methyl-2-pyrrolidone was purchased from Sigma-Aldrich. All solvents were degassed prior to use.

Instrumentation

Raman spectra were measured using a Renishaw 1000 Micro-Raman System equipped with a 514 nm laser operating at 1 mW. Atomic force microscopy was performed using a Bruker Multimode 8 instrument equipped with a silicon nitride cantilever tip. Samples for analysis in the (scanning) transmission electron microscope ((S)TEM) were prepared by drop casting dispersions onto lacey carbon grids. Between drop casting and imaging samples were stored under vacuum. TEM imaging was performed using an FEI Tecnai T20 operated at 200 kV. High resolution TEM (HRTEM) imaging, high angle annular dark field (HAADF) STEM imaging, and energy dispersive X-ray (EDX) spectrum imaging were performed using a probe side aberration corrected FEI Titan G2 80-200 S/TEM "ChemiSTEM™" instrument operated at 80 kV. EDX spectra and spectrum images were analysed using Bruker Esprit software and TEM and STEM images were analysed using Gatan Digital Micrograph and imageJ software. Mercury software was used to generate crystal structures of black phosphorus and phosphorene.

Exfoliation Procedure

Black phosphorous (75 mg) was added to *N*-methyl-2-pyrrolidone (15 mL). The suspensions were ultrasonicated in an Elmasonic P 70H bench-top ultrasonic bath (820 W across four horns) operating at 37 kHz frequency and 30% power for 24 or 48 h. The bath was modified by the addition of a water-cooling coil to control the bath temperature below 30 °C during sonication. Upon completion of the exfoliation step, an aliquot (5 mL) was removed and diluted with *N*-methylpyrrolidone (5 mL). The dispersion was centrifuged at a rate of 1500 rpm for 45 min to remove the remaining bulk material. The top two-thirds of the supernatant were collected for analysis. Dispersions were spin coated at 6000 rpm onto 300 nm SiO_2 on Si substrates using an Ossila spin coater for further analysis.

Supplementary Figures

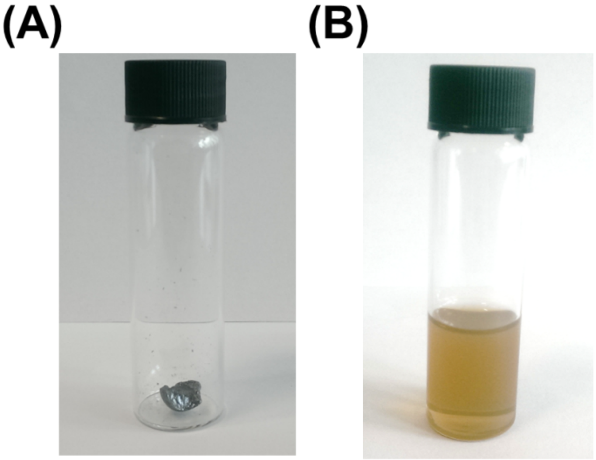

Fig. S1. Visual appearance of (A) black phosphorus and (B) exfoliated phosphorene sol in NMP after centrifugation steps.

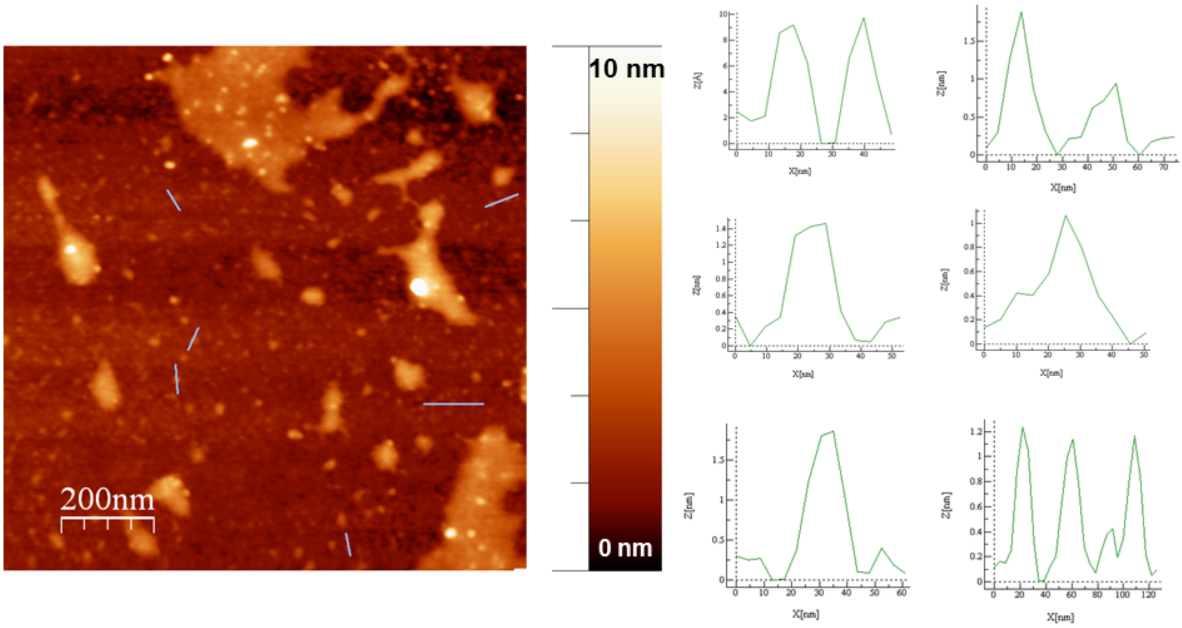

Fig S2. Atomic force microscopy height profile image of few-layer phosphorene sheets produced from ultrasonic exfoliation of bulk phosphorus in NMP for 24 h and spin-coated onto a SiO_2/Si substrate, with *z*-profiles of phosphorene flakes ($N = 10$) along the lines marked in the AFM image, suggesting predominantly 1-3 layer phosphorene (*ca.* 0.9 – 1.6 nm thickness), but with diminished lateral dimensions compared to the larger 3- 5 layer phosphorene nanosheets.

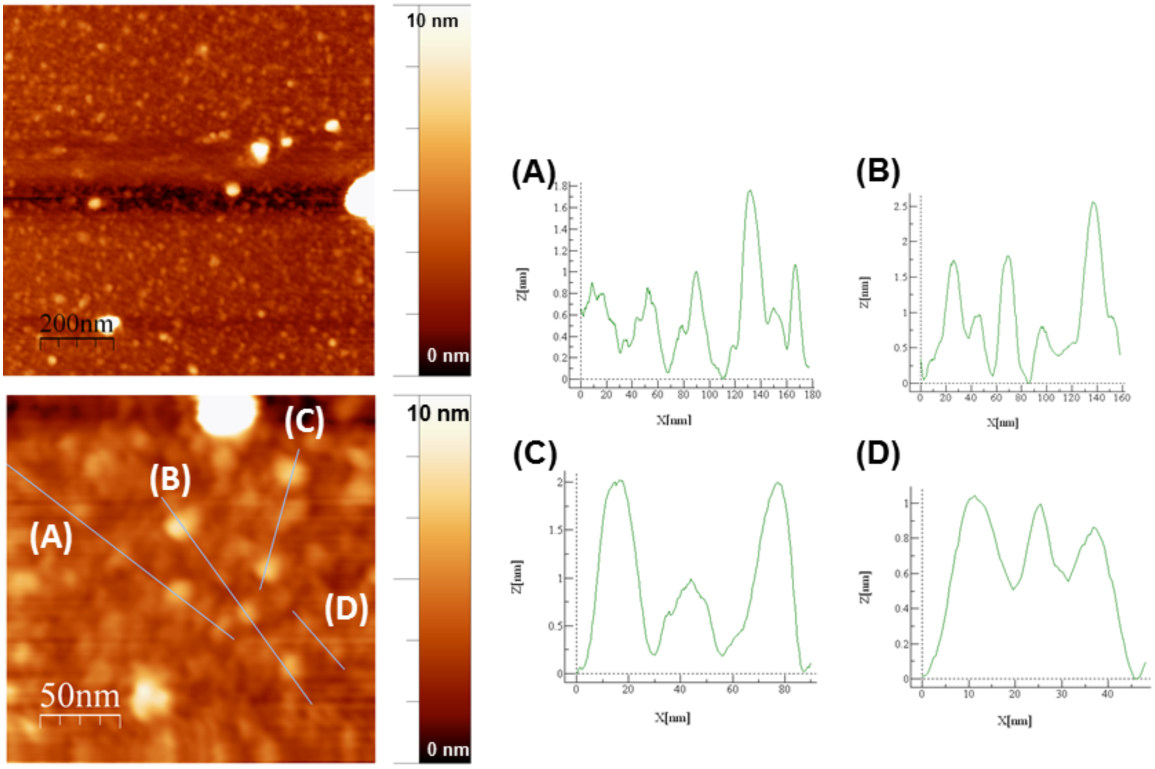

Fig S3. Atomic force microscopy height profile images of few-layer phosphorene sheets produced from ultrasonic exfoliation of bulk phosphorus in NMP for 48 h and spin-coated onto a SiO$_2$/Si substrate. (A), (B), (C) and (D) show *z*-profiles of phosphorene flakes ($N = 17$) along the lines marked in the lower AFM relief image, suggesting predominantly 1-3 layer phosphorene, but with diminished lateral dimensions (*ca.* 20 × 20 nm) compared to the sample exfoliated for 24 h.

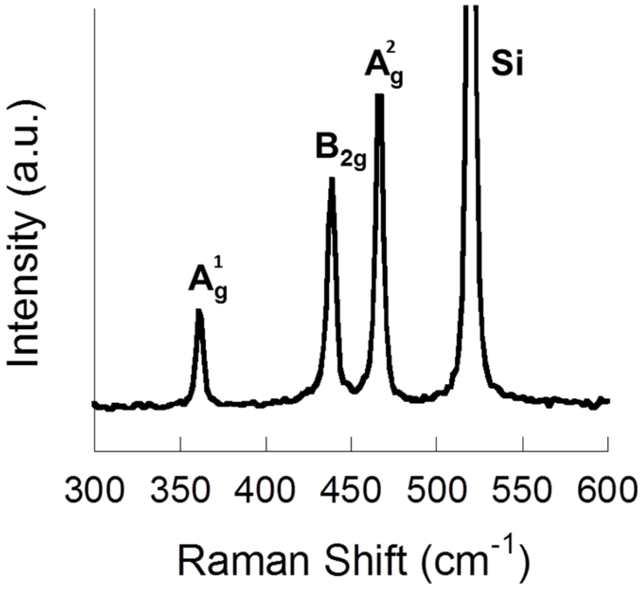

Fig. S4. Raman spectrum of few-layer phosphorene on SiO$_2$/Si substrate from liquid exfoliation of black phosphorus in NMP for 48 h showing the characteristic Raman bands at 362 cm^{-1}, 439 cm^{-1} and 467 cm^{-1} assigned to the A^1_g, B_{2g} and A^2_g modes.

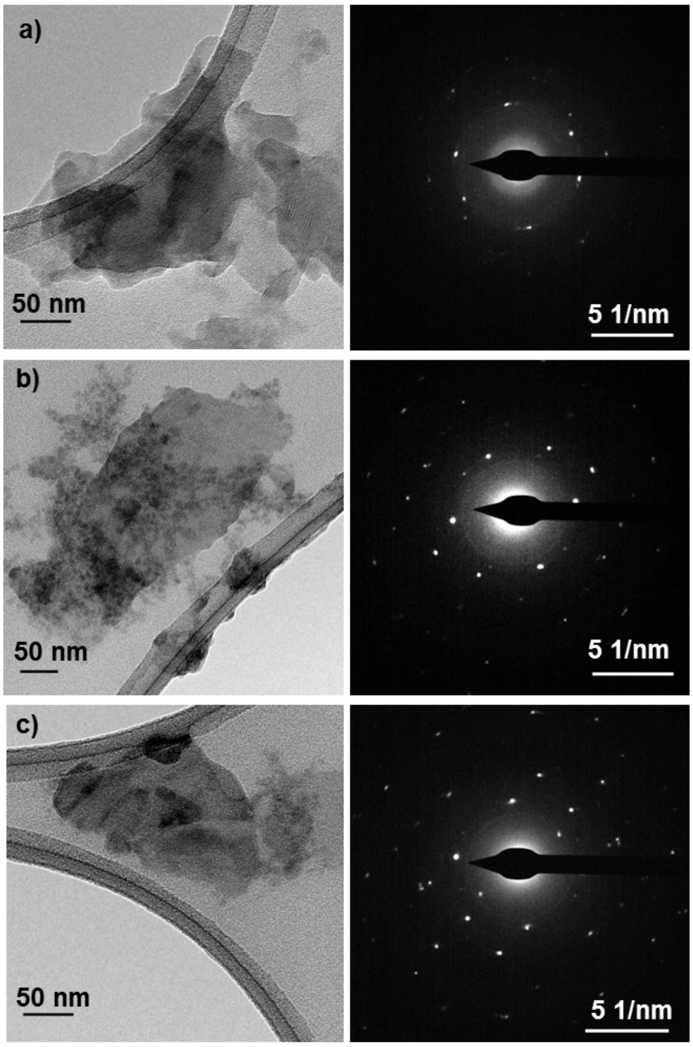

Fig. S5. Low magnification bright-field TEM images (left column) and corresponding selected area diffraction patterns (right column) for 3 typical flakes (a)-(c). Flakes show lateral dimensions greater than 100 nm. Diffraction patterns show that the flakes are highly crystalline.

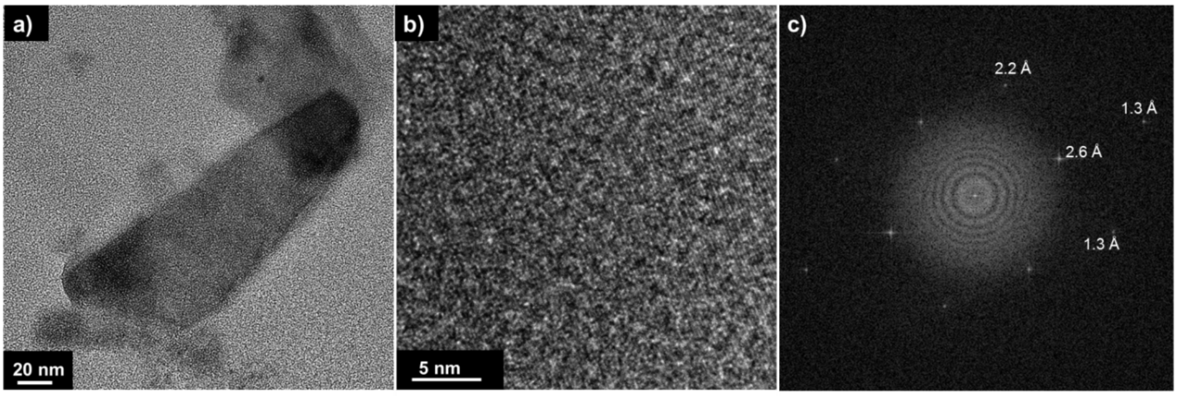

Fig. S6. High resolution electron microscopy of few-layer phosphorene. (a) Low magnification TEM image of a nanosheet, (b) HRTEM image of a region of this nanosheet. (c) Fast fourier transform of the HRTEM image.

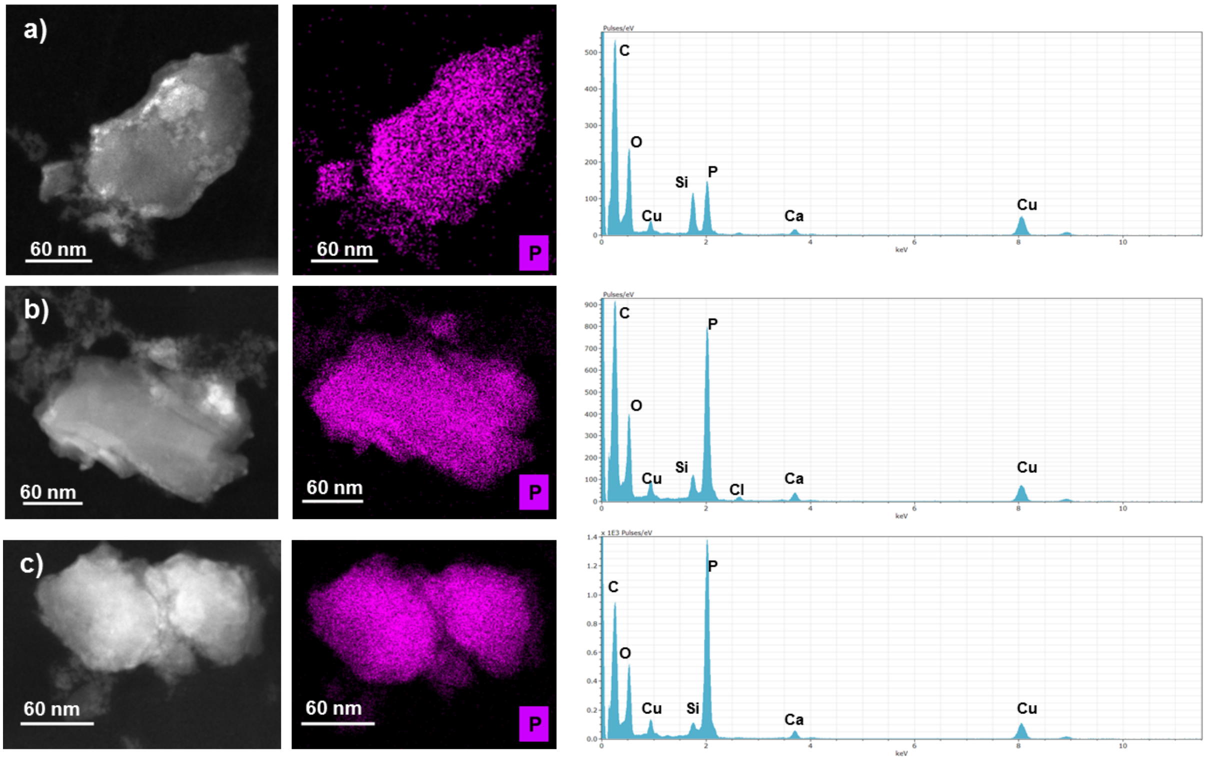

Fig. S7. EDX spectrum images were acquired for 3 different few-layer phosphorene nanosheets of typical size and morphology (a-c). Elemental maps were extracted from the spectrum images and EDX spectra acquired by summing over the spectrum images. HAADF STEM images of the flakes (left column) are presented alongside elemental maps for phosphorus (middle column), and EDX spectra (right column).