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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^{*ab} and Paul O'Brien^{*ab}

We report the liquid exfoliation of black phosphorus in *N*-methyl-2-pyrrolidone to form few-layer phosphorene nanosheets.

Graphene is the archetypal two-dimensional material.¹ Consisting of a single layer of covalently-bound sp²-hybridised carbon atoms,^{2,3} it has the potential to revolutionise many technologies as well as creating new ones. Graphene exhibits exceptional electronic properties,^{4–6} carrier transport⁷ and mechanical properties⁸ but lacks a band gap, making it of limited use in electronic devices without significant strain-engineering⁹ or physical modification of morphology.¹⁰ Due to its intrinsic band gap, molybdenum disulfide (MoS₂) has been considered as a potentially promising semiconductor for use in optoelectronics¹¹ and sensing¹² applications despite its relatively low carrier mobility.

Phosphorene,¹³ the two-dimensional variant of the layered black phosphorus allotrope (Fig. 1) has attracted attention due to its p-type semiconducting properties.¹⁴ *Ab initio* calculations predict that phosphorene has a direct thickness-dependent band gap of *ca.* 1.0 eV, corroborated by luminescence measurements, which is significantly larger than the band gap exhibited by bulk black phosphorus (*ca.* 0.3 eV).^{14–16} Additionally, phosphorene has high hole mobility.¹⁴ Hence, phosphorene has great potential for optoelectronic applications and use in semiconductor-based devices.

Micromechanical cleavage (Scotch tape delamination) has been shown to reliably produce pristine, ultrathin sheets of both graphene and phosphorene, as well as inorganic graphene analogues.^{6,14,17} Although the method is useful for small-scale production of two-dimensional materials for fundamental research purposes it is, by its nature, not a scalable process. Two options exist to



Fig. 1 The chemical structures of the compounds in this study. (A) The orthorhombic unit cell of black phosphorus¹⁹ ($a = 3.31 \text{ \AA}$, $b = 4.38 \text{ \AA}$, $c = 10.50 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$; space group *Bmab*; Crystallography Open Database ID: 1010325) which generates a layer structure comprising corrugated lamellae of phosphorus atoms held together by weak interlayer forces. (B) Three-layer phosphorene.

circumvent this problem. The first is by bottom-up large scale growth of two-dimensional materials, for example using chemical vapour deposition processes.¹⁸ The second is by top-down processes based on large-scale exfoliation of the bulk material precursor.

A number of successful syntheses of two-dimensional materials using liquid exfoliation have been reported by Coleman and co-workers including transition metal dichalcogenides (MoS₂, WS₂, MoSe₂, MoTe₂, TaSe₂, NbSe₂, NiTe₂), hexagonal boron nitride (h-BN) and bismuth telluride (Bi₂Te₃) as well as graphene.^{20,21} The layered bulk solid is immersed into a liquid, typically *N*-methyl-2-pyrrolidone (NMP), and the two-dimensional materials are ultrasonically exfoliated. The physical basis for the exfoliation relies on an energy match between the solvent and the surface of the two-dimensional material in question balancing the energy required for exfoliation. Shear exfoliation in liquids in the presence of detergents has also recently been shown to be a viable process for the large-scale production of two-dimensional materials.²² The size of sheets as well as the concentration of the colloid may be controlled by judiciously tuning the exfoliation conditions and isolation procedures.²³ Thus, liquid exfoliation routes are potentially appropriate for the large-scale production of two-dimensional nanomaterials with desired optoelectronic

^a School of Materials, The University of Manchester, Oxford Road, M13 9PL, UK.
E-mail: paul.o'brien@manchester.ac.uk, david.lewis-4@manchester.ac.uk;
Fax: +44 (0)161 275 4616; Tel: +44 (0)161 275 4653

^b School of Chemistry, The University of Manchester, Oxford Road, M13 9PL, UK
† Electronic supplementary information (ESI) available: Full description of exfoliation conditions, instrumentation used, visual appearance of black phosphorus and few-layer phosphorene dispersion; supplementary (S)TEM images, EDX spectra and EDX spectrum images. See DOI: 10.1039/c4cc05752j



properties, an essential requirement for a future electronics industry based on two-dimensional materials.

In this communication, we present a simple and scalable route to few-layer phosphorene nanosheets *via* liquid exfoliation of black phosphorus in NMP. The phosphorene sheets are characterised by Raman spectroscopy, atomic force microscopy (AFM), transmission electron microscopy (TEM), high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), energy-dispersive X-ray (EDX) spectroscopy and EDX spectrum imaging. To the best of our knowledge this is the first report of

the formation of colloidal dispersions of few-layer phosphorene nanosheets by liquid exfoliation.

To form phosphorene nanosheets, black phosphorus was exfoliated in NMP (5 mg mL^{-1} , $0.164 \text{ mol dm}^{-3}$ black phosphorus in NMP) using bath ultrasonication (820 W across four horns operating at 37 kHz frequency and 30% power) for 24 h. The temperature of the bath was maintained below 30°C throughout using a water cooling coil. Turbid dispersions were obtained from the exfoliation step that were further purified by centrifugation to remove larger solids (see ESI† for full exfoliation and purification details). Stable dispersions were obtained from purification which are pale yellow/brown in appearance (ESI†). Silicon substrates coated with silicon dioxide of *ca.* 300 nm thickness (SiO_2/Si) were spin-coated at 6000 rpm with a portion of the sol. Spin coating was used as the method of choice for preparation of the nanosheet-coated substrates to avoid aggregation and re-stacking of sheets. Raman spectroscopy (514 nm laser) of the spin coated SiO_2/Si substrates revealed Raman bands with maxima at 361 cm^{-1} , 438 cm^{-1} and 465 cm^{-1} , corresponding to the A_g^1 , B_{2g} and A_g^2 modes of few layer phosphorene, alongside the major scattering peak from the silicon substrate at 520 cm^{-1} (Fig. 2). These values do not suggest monolayer phosphorene was produced from exfoliation as reported by Ye and co-workers, but rather are akin to the values reported for bulk black phosphorus, suggesting that the flakes are comprised of ≥ 3 layers.

Atomic force microscopy (AFM) of exfoliated phosphorene on Si/SiO_2 substrates revealed the presence of a range of shapes and sizes of phosphorene, with flakes as large as *ca.* $200 \text{ nm} \times 200 \text{ nm}$ observed (Fig. 3). Height-profiling of large nanosheets revealed a thickness between *ca.* 3.5–5 nm ($N = 11$, Fig. 3A–D), with well-defined edges. Previous AFM measurements suggest that single-layer phosphorene has a thickness of *ca.* 0.9 nm.¹⁴ The AFM results suggest therefore that the large nanosheets



Fig. 2 Raman spectrum of few-layer phosphorene on a SiO_2/Si substrate from liquid exfoliation of black phosphorus in NMP showing the characteristic Raman bands at 361 cm^{-1} , 438 cm^{-1} and 465 cm^{-1} assigned to the A_g^1 , B_{2g} and A_g^2 modes.



Fig. 3 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. (A), (B), (C) and (D) show z-profiles of phosphorene flakes ($N = 11$) along the lines marked in the AFM relief image. Inset: (E) three-dimensional representation of the large *ca.* three-layer phosphorene flake observed at point (A).



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