Efficient and Fast Synthesis of Few-Layer Black Phosphorus via Microwave-Assisted Liquid-Phase Exfoliation

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High-quality, few-layer BP flakes have been prepared in a common organic solvent with very short processing times using microwave-assisted liquid-phase exfoliation. A comprehensive range of analysis, combined with density-functional theory calculations, confirmed that the product prepared using the microwave technique is few-layer BP with small- and large- area flakes. The suspended exfoliated BP sheets showed excellent stability, while samples dispersed onto silicon from the suspensions exhibited low oxidation levels after several days in ambient conditions. This straightforward synthesis method is facile, efficient and extremely fast, and does not involve use of any surfactant or ultrasonication steps and will facilitate future development of phosphorene research.

Phosphorene is a new member of the family of two-dimensional (2D) layered materials. In 2014, Zhang et al.[1] produced few-layer BP (FL-BP) from bulk BP inspiring researchers in diverse fields to explore the use of BP.[2-5] FL-BP exhibits unique properties such as high

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carrier mobility,[1, 2] excellent ON/OFF ratio,[2] high anisotropic properties,[6] and layer dependent band-gap[7, 8]. Although many investigations show promising results in different applications,[5, 9-11] the real success of phosphorene for practical applications will rely on finding a reliable and reproducible method of production.

Mechanical cleavage is used for the first demonstration of various 2D materials including graphene and phosphorene.[1, 2, 12] Although mechanically exfoliated BP has been widely used in many devices,[2, 13, 14] the labor intensive nature of this method restricts its commercial application. This method also suffers from other limitations such as lack of control of shape, size and thickness and instability under ambient conditions.[5]

Liquid-phase exfoliation (LPE) is a promising method that has been extensively used for the production of various ultrathin 2D materials.[15-17] This method has a number of advantages including solution processability, scalability, stability and a path to the preparation of composite materials.[18-20] Exfoliating bulk crystals in common solvents using ultrasonication is the most commonly used LPE method. However, in order to efficiently exfoliate the bulk BP into few-layer sheets, long processing times (>15 h) are usually required.[8, 21, 22] Such long sonication times are known to reduce the lateral size and create anomalous structural defects in the 2D nanosheets.[23] The limited number of established experimental procedures to produce phosphorene restricts its successful application.

Herein, we report a facile, novel and efficient method to produce solution processable FL-BP sheets using a microwave (MW)-assisted LPE method in ambient conditions. The as-prepared FL-BP flakes were highly crystalline, atomically thin and show low oxidation level in ambient condition. More importantly, our method requires a very short processing time (>12 min) and does not involve use of any surfactant or ultrasonication to obtain stable FL-BP.

Our LPE based on MW-assisted technique (**Figure 1**a) includes two-step microwaving processes using two different types of MW instruments. A detailed description of the processes is given in the Experimental Section. Briefly, the first microwaving step (termed

"MW–1") was expected to weaken the van der Waals interaction between BP layers. The second exfoliation step (called "MW–2") further exfoliates and separates the BP into a FL-BP sheets. Finally, the stable dispersion of FL-BP flakes is obtained after centrifugation. For the "MW–1", we found 50 $^{\circ}$C is the optimum parameter to efficiently exfoliate the BP among a range from 50 $^{\circ}$C to 120 $^{\circ}$C (**Figure S1**a). We also found that the combination of "MW–1" and "MW–2" is very effective in producing high-yield, FL-BP solution (**Figure S1**b). The mechanism of MW-exfoliation and other shear-exfoliation methods for 2D materials has been well described elsewhere.[24-26] Briefly, when MW irradiation is applied to the sample, van der Waals interaction between the bulk BP flakes starts weakening and further exfoliates layer by layer in the appropriate solvent.
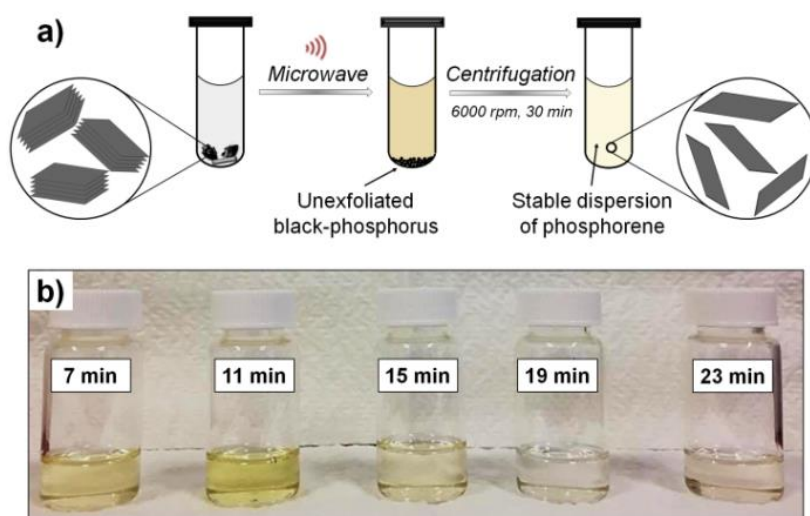

Figure 1. (a) Schematic for MW-assisted LPE of bulk BP flakes to produce FL-BP solutions. (b) Photographs of FL-BP solutions in NMP prepared by exfoliating bulk BP using different MW-exfoliation times.

The FL-BP dispersions were prepared by exfoliating bulk BP for different exfoliation times in "MW–1", always followed by the "MW–2" for 3 min. For comparison, bulk BP was exfoliated in NMP using bath sonication for 24 h to replicate previous studies.[8, 21, 22] **Figure**

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1b shows photographs of FL-BP dispersions obtained for different MW-exfoliation times. The dispersion color for 11 min MW-exfoliation is more intense than the other dispersions, indicating more efficient exfoliation and higher yield of FL-BP. Our FL-BP dispersion obtained by sonication showed a cloudy pale yellow color (**Figure S2**). As compared to the sonicated solution, a more intense yellow color of FL-BP dispersion prepared using MW-exfoliation suggests the production of high-quality FL-BP in N-Methyl-2-pyrrolidone (NMP).[8] However, as the MW time increases to 15 min, the yellow color started to disappear probably due to sample damage and NMP decomposition.

Figure 2a shows the optical absorption (in the NIR range) spectra of NMP-based FL-BP solutions prepared using different MW-times. For comparison, the absorption spectrum of the FL-BP dispersion prepared by the sonication is depicted in the inset of **Figure 2**a. Several spectral peaks were observed at around 1.38, 1.23, 1.05, 0.86, 0.72 and 0.64 eV (labelled 1-6) which can be associated with the fundamental bandgap values in one to six layers of phosphorene, respectively.[22] These peak energies are consistent with photoluminescence (PL) peaks reported for one to five layers of mechanically exfoliated BP.[27, 28] The smaller peak intensities at 1.38, 1.23 and 1.05 eV compared to other peaks indicate that the yields of one to three atomic layers of phosphorene are lower than other layers. The yield of the four and five layers MW-exfoliated BP flakes was comparable to that prepared using sonication based LPE.

Based on the peak intensity at 0.867 eV (4 layers), one can see that the FL-BP dispersion prepared using 11 min MW-exfoliation exhibited the highest absorbance (**Figure 2**a), indicating better yield. Short MW-exfoliation times were found to be insufficient, while long MW times seem to damage the samples. The scanning electron microscopy (SEM) image of the 7 min MW-exfoliated BP, in **Figure S3**, shows that such short processing time is insufficient to separate the BP layers into single or few layers. After the exfoliation for 7 min, the large BP sheets were found to start separating (see **Figure S3**) and a limited yield of FL-

BP was obtained. However, the absorption spectrum in the NIR (**Figure S4**) for a long MW time (23 min) showed negative peaks. We believe this is due to sample damage producing small phosphorene pieces (see SEM images in **Figure S4**). Moreover, Zhu et al.[25] recently reported the preparation of BP quantum dots (BPQDs) using a kitchen blender. They found that short processing time can produce nanosheets, but when longer processing time is used, the BP sheets disappeared and resulting in ultrasmall BPQDs. This finding is similar to what we observed from our samples when long MW processing time is used (**Figure S4**c).
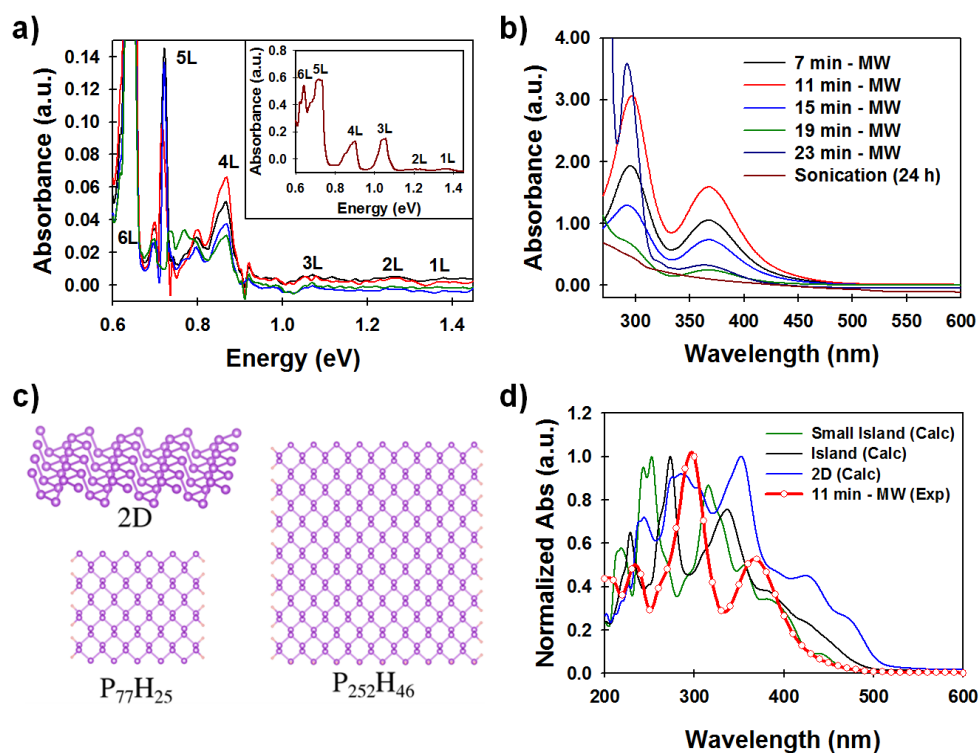

Figure 2. (a) NIR and (b) UV-vis spectra of FL-BP solutions prepared by different MW-exfoliation times. The inset shows the spectrum of the FL-BP solution prepared by 24 h sonication. (c) The atomic structure of the 2D monolayer structure and two H-passivated phosphorene clusters ($P_{77}H_{25}$ (small island) and $P_{252}H_{46}$ (island)). (d) Comparison of the absorption spectra of phosphorene in the UV-vis region obtained by DFT and experiment.

The FL-BP solutions were further examined using UV-vis spectroscopy (**Figure 2**b). Two main absorption peaks at around 300 and 370 nm were observed for all samples, which are consistent with previous results obtained from both the theoretical[29] and experimental investigations[7, 30]. Interestingly, the peak of our MW-exfoliated BP solutions at 370 nm was very strong and sharp as compared to that of the FL-BP dispersion prepared by sonication based exfoliation in this work (**Figure 2**b) and reported in previous studies.[7, 30] This strong and sharp peaks may indicate that the FL-BP sheets prepared using MW-exfoliation are very high-quality. Therefore, based on the absorption spectra of our samples across the NIR and UV-vis (**Figure S5**), we focused on the 11 min MW-exfoliated BP for further analysis.

Furthermore, we studied the UV-vis absorbance of phosphorene by performing density-functional theory (DFT) calculations within the generalized gradient approximation by Perdew, Burke and Ernzerhof (PBE)[31]. The optical absorption, $I(\omega)$ is computed as the imaginary part of the dielectric function in the linear response approximation,[32] and the optical absorbance is proportional to $\omega I(\omega)$.[33] These optical calculations are performed with an incident polarization along the zigzag direction (the average optical spectrum for the armchair and zigzag polarizations is qualitatively similar to the zigzag polarization; and therefore here we only adopt the zigzag polarization). We explore the periodic 2D monolayer structure and the two H-passivated phosphorene clusters, namely $P_{77}H_{25}$ (small island) and $P_{252}H_{46}$ (island), illustrated in **Figure 2**c. The spectra of these structures, in comparison with the experimental spectrum of 11 min MW-exfoliated BP, are displayed in **Figure 2**d. Generally, the UV-vis spectra of the three phosphorene structures qualitatively agree with the experimental spectrum in terms of possessing three characteristic peaks within the range 200-400 nm (centered at 230 nm, 300 nm and 370 nm in the experimental spectrum). In the three theoretical spectra in **Figure 2**d, we can clearly observe the trend in the positions of the spectral peaks as we go from the small island to the 2D phosphorene sheet: as the cluster becomes larger, the three characteristic peaks redshift towards their position in the 2D sheet.

However, an important distinction between the experimental spectrum and the 2D spectrum in the features of the three major peaks in the range 200-400 nm is that the rightmost peak at ~350 nm is higher in intensity than the other peaks. However, in the experimental spectrum, the middle peak (at ~300 nm) has the highest intensity, and this behavior is exhibited in the spectrum of the $P_{252}H_{46}$ cluster. Therefore, the synthesized phosphorene is simulated by large H-terminated phosphorene sheets with reasonable accuracy. Notably, these slight differences in the peak intensities and some peak shifts observed between the theoretical spectra and experimental spectrum are probably due to the fact that our FL-BP sample produced using MW-exfoliation method consists of few-layer to multi-layer and small- and large- area flakes, which are in excellent agreement with the other characterizations reported in this work. Very recently, Ahmed et al.[34] reported the UV-vis spectrum of mechanically exfoliated phosphorene layer, which was very consistent with our UV-vis spectra of FL-BP exhibiting two major peaks at around 300 nm and 370 nm. We also note that to the best of our knowledge, except our MW-exfoliated FL-BP, no experimental work on solution processed phosphorene has previously shown these three major peaks.

According to previous atomic force microscopy (AFM) studies,[2, 35] the thickness of single layer phosphorene is ~0.85 nm, which is slightly higher than that of the theoretical value (~0.6 nm)[2, 3]. The AFM results (**Figure 3**a and **3**b, **Figure S6** and **Table S1**) show that the measured heights of our FL-BP sheets vary from ~ 2 nm to ~15 nm, verifying that our sample consists of few layers to multilayers (2–18 layers) sheets. In line with the NIR results, yield of two layers phosphorene was low compared to few layers (4-6). When two layers are observed, they were typically situated at the edges of thicker flakes (**Figure S6**a). Based on the AFM height measurements in **Figure 3**b, we find the average thickness for all the flakes analyzed equal to 6.5 ± 2.6 nm. This yields a range of layer numbers from four to eleven while the range of layer numbers for the ultrasonicated sample was four to six (**Figure S7**).

Furthermore, the lateral size distribution of our FL-BP sample was investigated using SEM. It can be seen from **Figure 3**c that the lateral dimensions of our FL-BP ranged from hundreds of nanometers up to ~4 µm. We note that the large sheets observed in our MW-exfoliated BP are significantly bigger than those obtained using ultrasonication based liquid-exfoliated BP[8, 21, 22, 30] and comparable to those obtained using mechanical-exfoliation[1, 35].
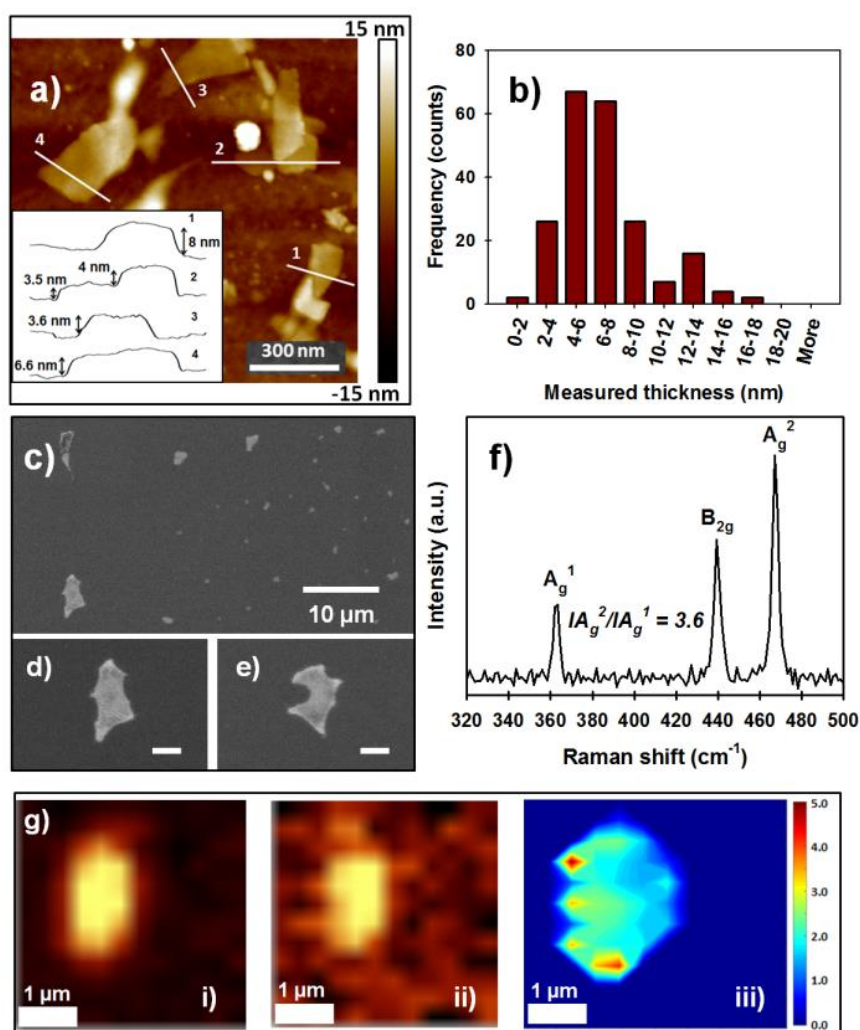

Figure 3. (a) AFM image of MW-exfoliated FL-BP. Inset shows the corresponding height profiles. (b) Histogram of heights taken from more than 200 measurements. (c-e) SEM images and (f) Raman spectrum of FL-BP sheets. Scale bars in (d) and (e) are 2.0 µm. (g) Confocal Raman images for the A_g^2 peak (i), A_g^1 peak ii) and A_g^2/A_g^1 (iii) ratio of the same flake.

A Raman spectrum of the MW-exfoliated FL-BP flakes is shown in **Figure 3**f. The Raman modes centered at 362.2 cm^{-1}, 439.4 cm^{-1} and 467.3 cm^{-1} can be assigned to the characteristic of A_g^1, B_{2g} and A_g^2 phonon modes, respectively, and are consistent with the signature Raman spectrum of the mechanically-exfoliated BP.[2, 36] However, compared to our bulk BP (**Figure S8**), no significant shift and change in the Raman spectrum was observed after 11 min MW-assisted exfoliation. Recently, Favron et al.[3] showed that there are no noticeable shifts in the three vibrational modes of the bulk BP where the phosphorene has more than four layers.

The ratio of the area under the peaks for the A_g^2 and A_g^1 bands can be used to determine the layer number of phosphorene sheets.[3, 35] Lu et al.[35] found that the A_g^2/A_g^1 ratio changed from 1.9 for bulk BP to 3.5 for three layers and increased to 10.5 for single layer. The A_g^2/A_g^1 integrated intensity ratio for the Raman spectra in **Figure 3**f is 3.6 suggesting three layers BP for this region. By mapping the A_g^2/A_g^1 ratio across a flake, approximate layer number over that flake can be determined. The Raman images in **Figure 3**g(i) and **3**g(ii) show the intensity maps of a flake for the A_g^2 peak and A_g^1 peaks, respectively, while the data in **Figure 3**g(iii) is a map of the A_g^2/A_g^1 integrated intensity ratio. The A_g^2/A_g^1 ratio varies from ~2 to ~4 across the flake, indicating the flake ranges from three to five layers at its thinnest to more than five layers in its thickest regions consistent with data from AFM and absorption spectra. Moreover, a signature for the degradation and/or oxidation of phosphorene from Raman spectrum is the emergence of a broad feature in the region under the B_{2g} and A_g^2 modes,[3] which is not observed in our sample demonstrating the structural integrity.

Scanning Auger microscopy can determine elemental composition with high spatial resolution as it combines SEM with Auger electron spectroscopy (AES). **Figure 4**a-d shows that the FL-BP flake under analysis has large lateral dimensions from 2 to 4 μm, which is consistent with the sizes observed in **Figure 3**c-g. The elemental mapping in **Figure 4**a-d indicates that our FL-BP sample on silicon substrate consists of three different elements, namely P, C and O. **Figure 4**e depicts the Auger electron spectroscopy (AES) for two locations on the flake.

Interestingly, the Auger spectrum obtained at the center of the flake showed only single "P" element (non-oxidized), while the edge of the flakes was partially oxidized (see **Figure 4**d). It has been reported that the oxidation starts to occur on the phosphorene from the edges of the flakes when exposed to air.[3, 5] The stability and degradation of FL-BP is the major challenge in phosphorene research and needs to be addressed with a great sense of urgency. Kang et al.[37] comprehensively investigated the stability of both mechanically-exfoliated and liquid-phase exfoliated BP based AFM and X-ray photoelectron spectroscopy (XPS).
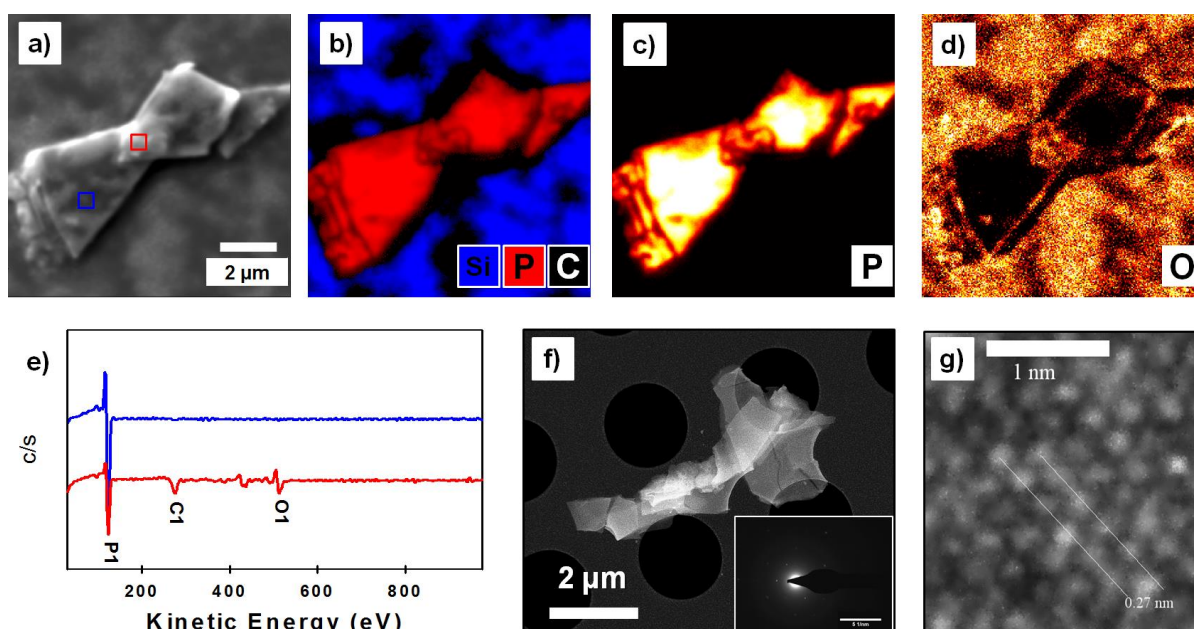

Figure 4. Auger elemental mapping and spectrum of FL-BP flake. (a) SEM image showing where the Auger maps were obtained. (b) Si (blue), P (red) and C (black) mapping, (c) P mapping and (d) O mapping. (e) The elemental spectrum corresponding to the two different locations (blue and red) as shown in (a). (f) TEM image of MW-exfoliated FL-BP. Inset shows the SAED pattern of the FL-BP. (g) High resolution TEM image of FL-BP nanoflake taken from a selected area in (f).

Transmission electron microscopy (TEM) was used to gain further insights into our FL-BP (**Figure 4**f and g). The majority of the sheets look transparent, indicating that they are ultrathin and are FL-BP sheets. As expected, the lateral sizes of the flakes were quite non-uniform, which further confirms that the MW-assisted LPE of bulk BP produces FL-BP sheets with the lateral sizes ranging from hundreds of nanometers to micron-scale. We further carried out selected area electron diffraction (SAED) (see Figure 4f inset) to confirm the high-quality single-crystal structure of our FL-BP which agrees well with previous reports of the crystal structure of FL-BP.[37, 38] High-resolution TEM of the sample in in Figure 4f exhibits the atomic structure of our FL-BP sheets, as shown in Figure 4g. The lattice spacing was measured to be ~0.27 nm, which is consistent with the previously reported values of single-layer and few-layer phosphorene.[22, 38]

This work points the way forward to reduce the processing time to make high quality, FL-BP from many hours to a few minutes. Considerable experiments are still required to explore the microwave parameters (time, power, temperature, etc.) to give the optimal yield of phosphorene. It may of course be that one set of conditions will give the largest amount of FL-BP while other conditions will be best to give single layer samples.

In summary, we have demonstrated efficient, facile and extremely fast production of high-quality, FL-BP flakes via MW-assisted LPE. We confirmed that the product prepared from the bulk BP using this MW technique is FL-BP nanosheets with thicknesses less than 10 nm. Both experimentally measured and theoretically calculated UV-vis spectra of the phosphorene consistently showed three major peaks, indicating efficient production of a phopshorene solution. The solution of our FL-BP flakes in a common organic solvent is well protected against degradation. The lateral dimensions of our FL-BP flakes prepared based on this novel method range from hundreds of nanometers up to ~4 µm. There is no doubt that this work will open up new possibilities for the preparation of thin films and hybrid materials based on

phosphorene in large-scale for a comprehensive range of applications including solar cells, batteries, supercapacitors, water splitting and so on.

Experimental Section

Materials: BP (99.998% pure) was purchased from Smart Elements. Unless otherwise specified, all chemicals were purchased from Sigma-Aldrich Co., Ltd., Australia and used as received.

Sample Preparation: A LPE method using MW-assisted technique includes two-step microwaving processes using two different types of MW instruments. The first MW (StartSYNTH Microwave Synthesis Labsta-tion, Milestone s.r.l) was operating with 600 W power and set temperature of 50 °C. The second MW step was carried out using CEM Discover SP – MW operating with a power of 220 W set temperature of 70 °C.

Firstly, 25 mg of bulk BP was immersed in 5 mL of NMP. The mixture was heated using the first MW system ("MW-1") for different periods of time ranging from 4 min to 20 min, followed by treatment with the second MW ("MW-2") for 3 min. Then, a supernatant (4 mL) was taken and centrifuged at 6000 rpm for 30 min. After centrifugation, the top 70% of the solution was collected for further analysis and application. Finally, the stable dispersion of FL-BP flakes was obtained after centrifugation.

Supporting Information
Supporting Information is available from the Wiley Online Library.

Conflict of Interest
The authors declare no conflict of interest.

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Facile and fast production of high-quality, few-layer black phosphorus sheets via a microwave-assisted liquid-phase exfoliation method is demonstrated.

Keyword: 2D Materials, black phosphorus, liquid-phase exfoliation, microwave synthesis

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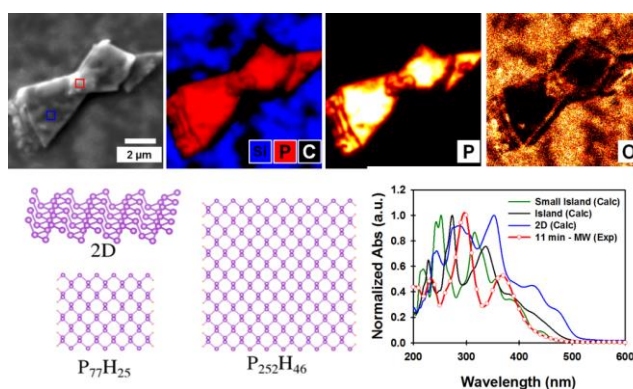
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Supporting Information

Efficient and Fast Synthesis of Few-Layer Black Phosphorus via Microwave-Assisted Liquid-Phase Exfoliation

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Characterization.

The optical absorption of the as-prepared dispersions of few-layer BP flakes was analyzed using a UV-vis-NIR spectroscopy (Perkin Elmer Lambda 950) at wavelengths ranging from 200 nm to 2200 nm. It should be noted that the optical absorption measurements were carried out after the subtraction of MW-treated NMP as the background. For example, for the optical absorption of 11 min MW-exfoliated few-layer BP solution, the background solvent (NMP) without BP was treated using MW technique for 11 min and used for the background subtraction.

Atomic force microscopy (AFM) was performed in air using either a Bruker Dimension FastScan AFM with Nanoscope V controller, operating in Peak Force Tapping mode or a Bruker multimode AFM with Nanoscope V controller, operating in standard tapping mode. Peakforce tapping mode images were acquired using Bruker ScanAsyst-air probes (nominal tip diameter and spring constant is 4 nm and 0.4 N/m respectively) and for tapping mode the probes used were silicon HQNSC15/AlBS Mikromasch probes (nominal tip diameter and spring constant is 16 nm and 40 N/m respectively). Set-point, scan rate and gain values were chosen to optimize image quality and flake thickness using procedures outlined by Shearer et al.[1] for Peakforce tapping mode and Nemes-Incze[2] for standard tapping mode. The AFM topography images have been flattened and thickness measurements were made using the section analysis tool of Nanoscope Analysis 1.4. For AFM analysis, the samples were prepared by spin coating the as-prepared solutions onto cleaned silicon substrates at 3000 rpm for 20 s. Scanning electron microscopy (SEM) images were obtained using an Inspect F50 SEM (FEI) with accelerating voltage of 5.0 kV.

Raman spectra were acquired using a Witec alpha300R Raman microscope at an excitation laser wavelength of 532 nm with a 40x objective (numerical aperture 0.60). Typical integration times for single Raman spectra were between 30-60 s for 2-3 accumulations. Confocal Raman images were also acquired with integrations between 1 to 6 seconds per pixel. Each pixel in the Raman images represents a Raman spectrum with the number of pixels in a typical Raman image representing hundreds of spectra. Confocal Raman images are generated by plotting the intensity of a specified region of each Raman spectrum that corresponds to a material, versus the X-Y position of the excitation laser as it scans the sample surface. The highest resolution grating available on the instrument was used which was 1800 grooves mm^{-1}. This grating has a spectral resolution of ~1 wavenumber which is insufficient to resolve the peak shifts expected for four layers or less phosphorene compared to BP as has been noted by numerous research groups.[3-5] Laser power levels were kept as low as possible to prevent sample damage.[6] The power was approximately 1 mW or below.

Auger electron spectroscopy (AES) (including elemental mapping) and simultaneous Secondary Electron Microscopy was performed on a PHI710 Scanning Auger Nanoprobe. The vacuum pressure in the analysis chamber during analysis was maintained at approximately 10^{-10} Torr. A 10 kV electron beam with a beam current of 10 nA was used to produce SEM images and AES data. Elemental maps were obtained at either 512 x 512 or 256 x 256 pixel resolution. Bright-field transmission electron microscopy (TEM) images were acquired using a FEI Titan Themis at 80kV accelerating voltage. Samples were dispersed by drop-casting onto quantifoil SQR12-200CU grids at 80ºC in air for ~2 mins until dry, and then immediately transferred to high vacuum storage prior to analysis.

Density-functional theory (DFT) calculations.

We perform our density-functional theory (DFT) calculations with the Perdew-Burke-Ernzerhof exchange-correlation functional,[7] using the SIESTA code.[8] We perform geometry relaxation to obtain the ground state electronic structure at the Γ point, where the simulation box is 40 Å x 40 Å x 20 Å. SIESTA represents the basis sets in terms of numerical atomic orbitals, and approximates the ionic potential in terms of Troullier-Martins[9] norm-conserving pseudopotentials. The auxiliary basis uses a real-space mesh with a kinetic energy cutoff of 300 Ry, and the basis functions are radially confined using an energy shift of 0.005 Ry. In the structural energy minimization, the internal coordinates are allowed to relax until all of the forces are less than 0.01 eV/ Å.
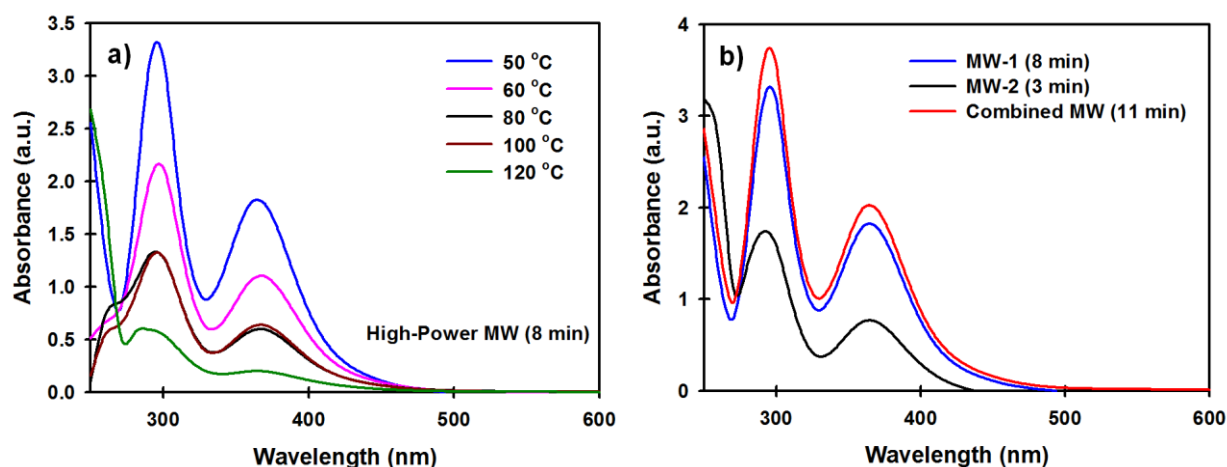

Figure S1. UV-vis spectra of few-layer BP in NMP prepared using (a) MW-1 only at different temperatures for 8 min, and (b) MW-1 (8 min), MW-2 (3 min) and their combination.

Figure S2. Photograph of few-layer BP in NMP prepared by exfoliating bulk BP using ultrasonication for 24 h.
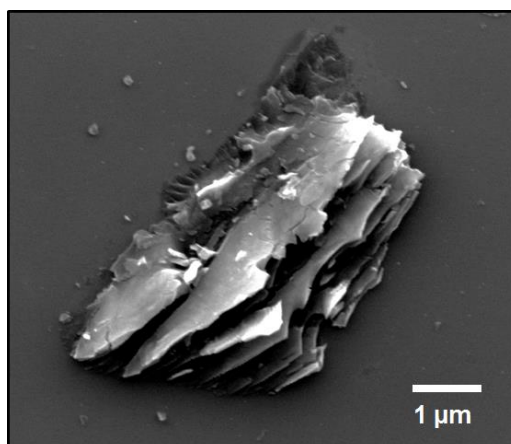
Figure S3. SEM image of MW-exfoliated BP in NMP for 7 min.
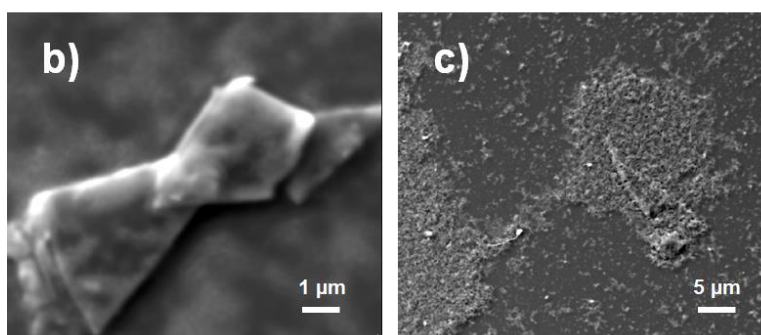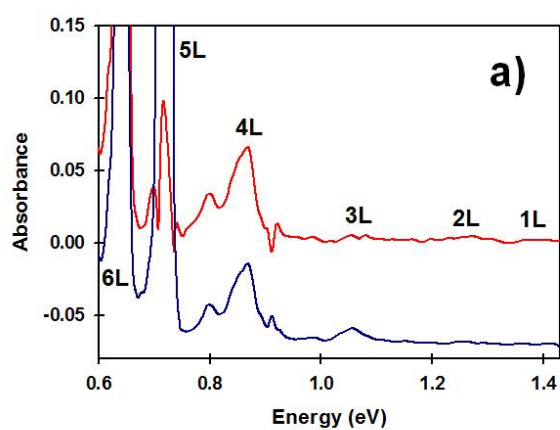

Figure S4. (a) Optical absorption spectra of few-layer BP solutions in the NIR region. SEM image of BP flakes after MW treatment of (b) 11 min and (c) 23 min.
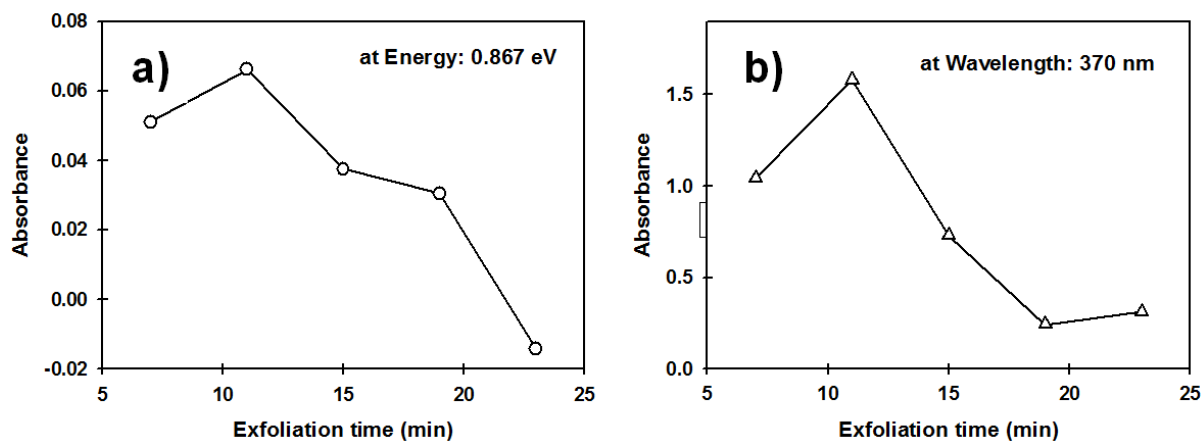
Figure S5. Optical absorption of few-layer BP solutions prepared using different MW-exfoliation times at the wavelength of (a) 1430 nm (NIR range) and (b) 370 nm (UV-vis range).
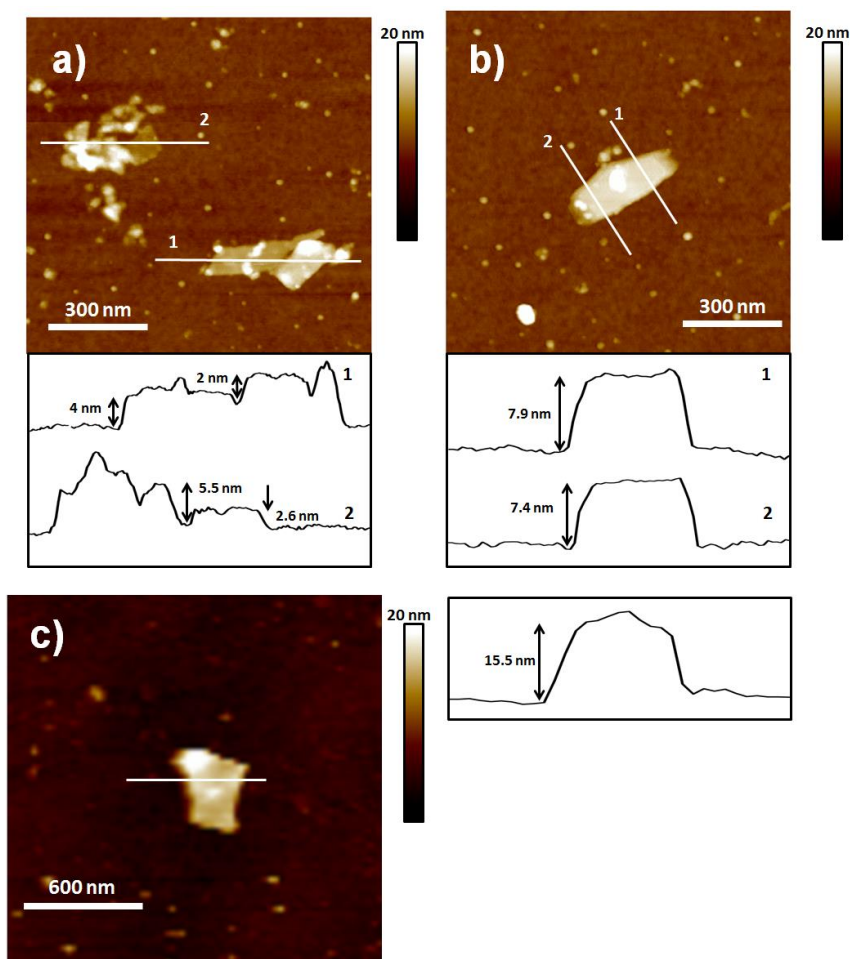

Figure S6. AFM images of few-layer BP sheets prepared using 11 min MW-assisted exfoliation method.

Table S1. Histogram of heights measured on 16 different phosphorene flakes produced using 11 min MW-exfoliation of bulk BP. These measured height values are used to plot Figure 2b in the main manuscript. Error is one standard deviation.

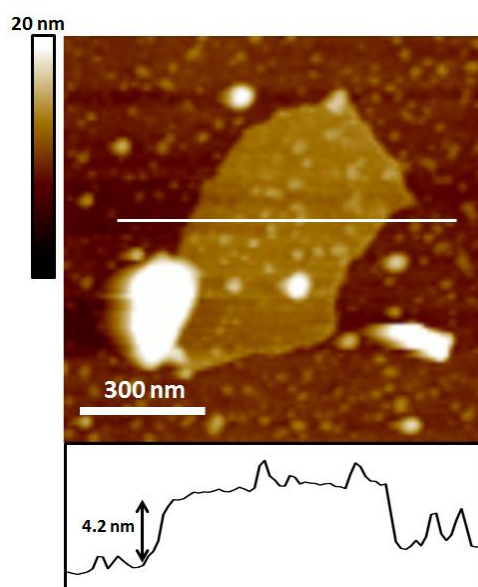| Flake number	N = number of measurements	Thickness using section analysis.	Approximate layer number assuming 1 layer = 0.85 nm
1	10	7.5 ± 0.6	8 to 10
2	9	4.3 ± 0.84	4 to 6
3	6	5.2 ± 0.4	6
4	7	3.6 ± 0.93	3 to 5
5	7	4 ± 0.7	3 to 5
6	10	8.5 ± 1.4	8 to 12
7	10	7.1± 1.5	6 to 10
8	10	9.1 ± 3.4	7 to 15
9	12	4.9 ± 0.5	5 to 7
10	15	6.7 ± 0.5	7 to 9
11	15	2.8 ± 0.7	2 to 4
12	31	7.4 ± 1.3	7 to 10
13	17	8.1 ± 1.6	8 to 11
14	17	5.7 ± 1.2	5 to 8
15	19	5.7±1.0	5 to 8
16	19	14.0 ± 1.5	15 to 18

Figure S7. AFM image and corresponding height measurement of few-layer BP sheet prepared using ultrasonication based liquid exfoliation. The average thickness of bath sonicated (24 h) phosphorene flake was 4.5 ± 0.7 nm (from 16 measurements), which is 4 to 6 layers assuming 1 layer of phosphorene is approximately 0.85 nm.
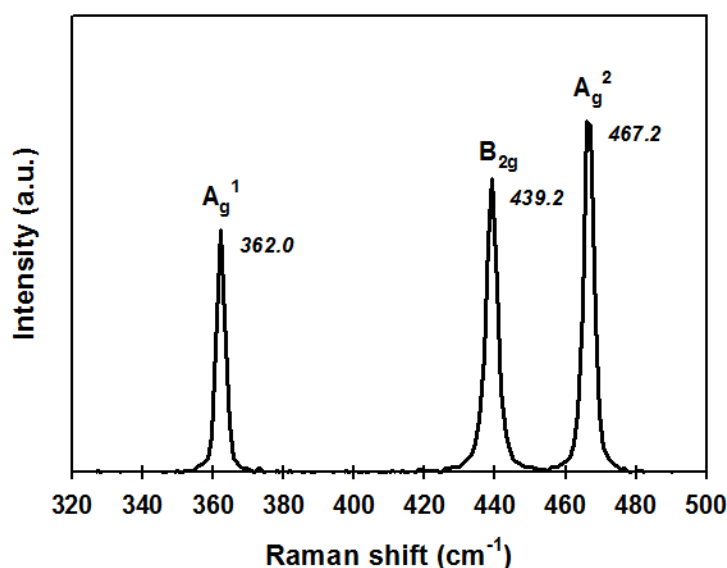
Figure S8. Raman spectrum of the bulk BP before the exfoliation. It should be noted that the A_g^2/A_g^1 ratio we measured for our bulk BP (starting material) was approximately 1.4 which is an average from ~ 100 measurements.

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