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***In situ* TEM Visualization of Superior Nanomechanical Flexibility of Shear-Exfoliated Phosphorene**

Feng Xu,^{†*a,b} Hongyu Ma,^{†c} Shuangying Lei,^a Jun Sun,^a Jing Chen,^d Binghui Ge,^{*e} Yimei Zhu^b and Litao Sun^{*a,f}

^aSEU-FEI Nano-Pico Center, Key Laboratory of MEMS of the Ministry of Education, Southeast University, Nanjing 210096, China. E-mail: fxu@seu.edu.cn; slt@seu.edu.cn

^bCondensed Matter Physics & Materials Science Department, Brookhaven National Laboratory, Upton, New York 11973, USA

^cResearch Center for Internet of Things, China University of Mining and Technology, Xuzhou 221008, China.

^dSchool of Electronic Science & Engineering, Southeast University, Nanjing 210096, China

^eBeijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China. bhge@iphy.ac.cn

^fCenter for Advanced Materials and Manufacture, Joint Research Institute of Southeast University and Monash University, Suzhou 215123, China.

[†]These authors contributed equally to this work.

ABSTRACT: Recently discovered atomically thin black phosphorus (called phosphorene) holds great promise for applications in flexible nanoelectronic devices. Experimentally identifying and characterizing nanomechanical properties of phosphorene are challenging, but also potentially rewarding. This work combines for the first time *in situ* transmission electron microscopy (TEM) imaging and *in situ* micro-manipulation system to directly visualize the nanomechanical behaviours of individual phosphorene nanoflakes. We demonstrate that the phosphorene nanoflakes can be easily bent, scrolled, and stretched, showing remarkable mechanical flexibility rather than fracturing. Out-of-plane platelike bending mechanism and in-plane tensile strain of up to 34% were observed. Moreover, a facile liquid-phase shear exfoliation route has been developed to produce such mono-layer and few-layer phosphorene nanoflakes in organic solvents only using a household kitchen blender. Effects of surface tensions of the applied solvents on the ratio of average length and thickness (L/T) of the nanoflakes were studied systematically. The results reported here will pave the way for potential industrial-scale applications of flexible phosphorene nanoelectronic devices.

Introduction

Success in mechanically exfoliating graphene^{1,2} and transition metal dichalcogenides (TMDs)^{3,4} has triggered a booming research on exploring new layered two-dimensional materials (LTMs).⁵⁻⁷ Recently discovered phosphorene is just a case in point.^{8,9} Phosphorene, mono-layer or few-layer black phosphorus (BP) atomic layer(s), holds great promise to be an alternative 2D semiconductor material due to its high carrier mobility (up to $10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),¹⁰ thickness-dependent tunable direct bandgap,¹¹ large $I_{\text{on}}/I_{\text{off}}$ ratios ($\sim 10^4$ – 10^5),⁸ and anisotropic properties.^{12,13} Structurally similar to graphite and TMDs, stacking BP atomic layers by weak interlayer forces with significant van der Waals character, makes mechanical exfoliation for small-scale high-quality phosphorene a reliable laboratory-level technique.¹⁴ Alternatively, liquid-phase exfoliation by virtue of sonication energy has been utilized to prepare

electronic-grade phosphorene nanoflakes.^{15–17} However, the scalability of the method is limited by the utilization of sonication as an energy source. Therefore, in order to progress from the laboratory to commercial applications, developing alternative methods that have ability to produce high-quality phosphorene nanoflakes on a large scale is still of great necessity.

Moreover, one particularly promising application for phosphorene could be flexible electronics due to its strong interatomic covalent bonding and excellent theoretical mechanical flexibility.¹⁸ In this regard, flexible electronic devices such as graphene field-effect transistors,¹⁹ MoS₂ gas sensors,²⁰ MoSe₂ and SnS₂ photodetectors,^{21,22} and graphene-WS₂ heterostructure transistors²³ have emerged in succession. Theoretical studies have also been performed to better understand concomitant mechanical behaviours when handling the flexible devices. Using density functional theory, Marianetti *et al.*²⁴ studied mechanical failure of graphene under tension and revealed phase transition-induced reduction of strength. Feng *et al.*²⁵ employed first-principles calculations to analyze elastic properties of WS₂ under pressure. When applying phosphorene in flexible devices in the future, it will also be necessary to understand its mechanical durability and reliability against adventitious strain. However, so far there have been no experimental works regarding the mechanical behaviour of the phosphorene under bending and scrolling conditions. The existing theoretical works mainly focus on in-plane mechanical properties such as poisson's ratio and tensile strain.^{26,27} How will the phosphorene behave under the large bending conditions? Will it lose structural stability or fracture under severe scrolling deformation? Will its mechanical properties be found for unique puckered structure? These concerns call for a direct microscopic investigation of phosphorene at the nanoscale.

In this paper, we first report a scalable shear-exfoliation method to prepare high-quality mono-layer and few-layer (<8 layers) phosphorene nanoflakes in liquids by a household kitchen blender that can generate enough shear-force to break down interlayer van der Waals forces of the bulk BP crystals, as shown in Fig. 1a. The shear-exfoliated phosphorene nanoflakes (SPNs) exhibit properties competitive to the mechanically exfoliated counterparts. To the best of our knowledge, this is the first report of phosphorene nanoflakes produced by the liquid-phase shear-exfoliation method. More importantly, we combine *in situ* transmission electron microscopy (TEM) imaging and *in situ* micro-manipulation system (Fig. 1b) to directly visualize the nanomechanical behaviours of the SPNs during bending, scrolling, and stretching. We demonstrate that the SPNs can be easily bent, scrolled, and stretched, showing remarkable in-plane and out-of-plane mechanical flexibility rather than fracturing. This direct microscopic observation for the phosphorene not only proves its potential applications in flexible electronics, but also serves to better understand its nanomechanical deformation mechanism.

Experimental

Shear-exfoliation preparation of the SPNs

Bulk BP was purchased from Smart Elements and was kept in a glove box filled with Argon gas prior to use. The SPNs were prepared by the turbulence-assisted shear-exfoliation²⁸ of bulk black phosphorus (BP) crystal in a household kitchen blender (model JYL-G11). At a rated power input of 250 W, the rotating blades (6 cm in diameter) can generate rotation speeds of 15500–22000 rpm. In a typical experiment, 200 mg of bulk BP crystals were put into the kitchen blender with 200 mL *N*-cyclohexyl-2-pyrrolidone (CHP) solvent. Upon pressing the power button, the blender began to work at the rated input power for a predetermined time of 40 min. The blender can generate violent turbulence flow to break down the interlayer van der Waals forces of bulk BP. The CHP solvent gradually turn black/brown colour as the BP starts to delaminate under the high-shear turbulence flow, eventually forming dispersions of the SPNs. A schematic diagram showing the exfoliation process from bulk BP crystal to SPNs is illustrated in Fig. 1a. After exfoliation, the as-obtained dispersion was isolated by centrifugation at a speed of 2000 rpm. Then, top 50% of the supernatant was collected and washed twice with IPA by centrifugation at a speed of 13000 rpm to remove CHP solvent. Ultimately, the supernatant was removed and the precipitate was re-dispersed in IPA for subsequent characterization and analysis.

Other solvents *N*-methyl-pyrrolidone (NMP), 1,4-dioxane, dimethyl sulfoxide (DMSO), dimethylacetamide (DMAC), dimethylformamide (DMF), and isopropanol (IPA) were also used for exfoliation.

Characterization of the SPNs

The SPNs were characterized using an aberration-corrected JEOL ARM-200CF transmission electron microscope (TEM) operating at 80 keV to minimize possible electron-beam induced damage. For sample preparation, the SPN dispersions in IPA were drop-cast on a lacey carbon TEM grid (Ted Pella, Inc.) that was then loaded onto the double-tilt TEM holder in Ar-gas glove box. The holder was taken out and immediately inserted into the TEM within one minute. High-resolution TEM images of both mono-/few-layer BP were simulated using XHREM software (version 3.9.0). The thickness of the SPNs was assessed using atomic force microscopy (AFM) ScanAsyst mode recorded using a MultiMode 8 AFM microscope (Bruker) with Si₃N₄ tip and processed using NanoScope Analysis software. AFM samples were prepared in an Ar glove box by spin-coating the SPN dispersions onto 200 nm SiO₂-coated silicon substrates, and then stored in Ar gas-filled sealing bags until AFM characterization. Scanning electron microscopy (SEM) was performed using a field emission scanning electron microscope (FESEM, JSM-7600F, JEOL, Japan). Raman spectroscopy was performed using a HRC-10HT Raman Analyzer (Enwave Optronics Inc.) The excitation wavelength was 785 nm with 1.0 mW focused on individual SPNs using a 100×microscope objective.

In situ TEM visualization of mechanical properties of the SPNs

In situ nanomechanical properties of the SPNs were investigated inside a transmission electron microscope (Titan80-300, FEI) using a state-of-art scanning tunneling microscopy (STM)-TEM sample holder (Nanofactory Instruments) with a piezo-tube driven manipulator. An electrochemically etched tungsten (W) tip was mounted onto the movable manipulator (STM probe) that can be driven in 3D directions with nanometer precision under the piezo-tube's drive. The SPNs were tightly glued to the edge of a counter Cu grid, which was set onto the fixed terminal facing the moveable W tip, as shown in Fig. 1b. Under TEM observations, individual SPNs protruding from the Cu grid edge were first selected. Under the control of the manipulator, the nanoscale W tip was driven to contact with the free end of the protruded SPNs. By manipulating the W tip in 3D, the bending, scrolling, and stretching of the SPNs were captured and recorded by a high-performance Gatan CCD (Model 894).

Results and discussion

Fig. 2a shows a typical TEM image of an ultrathin SPN on a lacey carbon film. Schematic diagram of atomic structure of mono-layer phosphorene along top-view projection is also inset in Fig. 2a. Structurally, bulk BP consists of P atoms stacked in puckered subplanes, and each P atom is bonded with two adjacent atoms lying in the same plane and with one P atom from another different plane. Here, our mono-layer phosphorene exfoliated from bulk BP is clearly resolved by HRTEM imaging and corresponding SAED pattern along [010] projection, as shown in Fig. 2b and c. A filtered section of the HRTEM image (inset in Fig. 2b) further shows atomic-level structure characteristic of mono-layer phosphorene, which obviously is different from the stable AB or metastable Aδ stacking orders in our recent theoretical study of few-layer phosphorene.²⁹ Moreover, we also used XHREM software to perform TEM simulations (viewing from the [001] direction) on mono- and few-layer phosphorene structures (Fig. S1). The simulated mono-layer structure perfectly matches the imaged HRTEM image, further corroborating successful exfoliation of the mono-layer phosphorene. These TEM analyses provide strong evidence that high-quality SPNs with highly crystalline nature can be facilely produced by liquid-phase shear-exfoliation in CHP using the simple blender.

Chemical purity of the SPNs is inspected by the EDS analysis. Comparison between HAADF-STEM image (Fig. 2d) and EDS mapping images (Fig. 2e and f) indicates high purity of the as-prepared SPNs, no obvious carbon residual from organic solvent is found on the surface of the SPNs. The chemical quality of the SPNs is further checked by EELS (Fig. 3a and b). The invisible plasmon peak in low-loss EELS (Fig. 3a) proves that the SPN is so thin that the plasmon

signal cannot be detected effectively.³⁰ The characteristic core-loss peak at 133 eV corresponding to the P $L_{2,3}$ edge is observed clearly (Fig. 3b). Absence of the signal P_xO_y peak confirms the pure P elementary substance on the whole SPN. Raman spectrum of the SPNs on Si substrate was performed (Fig. 3c). Four modes are observed at 363 cm^{-1} , 438 cm^{-1} , 465 cm^{-1} , and 523 cm^{-1} assigned to the A_g^1 , B_{2g} , and A_g^2 phonon modes for the SPNs and the TO phonon mode for the Si substrate, respectively. The Raman spectrum is well in accord with the previous report of the mechanically exfoliated counterparts,³¹ providing strong evidence that the SPNs maintain highly crystalline nature.

For further size and thickness analyses, the SPNs were characterized by AFM and SEM. AFM samples were prepared in an Ar glove box by spin-coating the SPN dispersions onto 200 nm SiO_2 -coated silicon substrates and then were stored in Ar gas-filled sealing bags until AFM characterization. An individual SPN is imaged by AFM, as shown in Fig. 4a. Step heights of 3–3.7 nm indicate few-layer-thick (<8 layers) SPNs produced by the shear-exfoliation method. No obvious bubbles, droplets, or other signs of the degradation are found for the SPNs. For SEM characterization, the SPN dispersions were firstly filtrated by polytetrafluoroethylene (PTFE) membrane. The stacked SPNs on the PTFE membrane exhibit irregular morphologies with several microns in size (Fig. 4b and c). Further statistical analyses of length (L) and thickness (T) distributions of the SPNs were studied by large quantities of TEM and AFM observations. Average L of $4.1\text{ }\mu\text{m}$ and average T of 2.25 nm were obtained, as shown in Fig. 4d and e. Although the fraction of mono-layer phosphorene observed is not very high, most of the SPNs have eight or less layers. The statistical results confirm the successful exfoliation with a dominance of mono-layer to few-layer phosphorene nanoflakes in organic liquids.

To test the effect of solvents on the quality of the SPNs, we prepared a range of dispersions in different solvents such as NMP, 1,4-dioxane, DMSO, DMAC, DMF, and IPA, but keeping all of the shear-exfoliation parameters constant. More than 100 SPNs of every sample were randomly selected and analysed by AFM and TEM observations to obtain the distributions of the L and T . Their typical TEM images and statistical results are shown in Fig. 5. From TEM characterizations, the shear-exfoliation of the SPNs could be achieved in all these solvents. However, statistical results show different average L and T of the SPNs for these solvents. High average L of $4.8\text{ }\mu\text{m}$ was obtained for the NMP and DMSO solvents, while the SPNs with low average T of 2.6 nm and 2.8 nm were prepared in the DMAC and DMF, respectively. Combining Fig. 4d and e with Fig. 5, we find that the average L of the SPNs shows a rising trend with increasing the surface tensions of applied solvents, as shown in Fig. 5g. Interestingly, the value of average T rises first and then drops (Fig. 5h). From the perspective of pragmatic applications, the SPNs with larger length and thinner thickness should be desirable. Therefore, the ratio of average L and average T is used to evaluate the quality of the SFNs. Fig. 5i gives the changes of L/T ratios of the SPNs as a function of surface tensions of the solvents. Obviously, the CHP, DMAC, and DMF are more suitable for preparing the SPNs with high L/T ratios. In previous liquid-phase sonication exfoliations of other 2D materials exclusive of phosphorene, Ajayan *et al.* found that exfoliation efficiency was enhanced when the ratios of the surface tensions components of the applied solvents was close to those of the 2D materials.³² To a certain extent, their finding can be also used for reasonably explaining why some solvents are better for the shear-exfoliation of high-quality SPNs in our cases.

Successive TEM images of the *in situ* bending behaviour of a SPN are shown in Fig. 6. The contact between W tip and SPN first resulted in slight bending that immediately introduced adventitious strain along the nanoflake (Fig. 6a and b); the asymmetrical strain distribution caused the striated contrast. This is because that the contact with the W probe prohibits interlayer sliding of the SPN layers under bending, as observed in the bending of few-layer MoS_2 .³³ Note that the strain induced fringes gradually propagated to the upper end of the SPN and converged in the frame region (Fig. 6c). This implies that adventitious strain could not be released because the upper end of the flake was fixed to the Cu grid by silver glue. The converged strains evolved into the characteristic dark fringe by further bending the SPN, as shown in Fig. 6d and e. Due to lack of proof of interlayer sliding, it is hard to say that the dark fringe is a kink. Maybe, it is just a simple bend partially out of plane that gives the illusive appearance of a kink. Generally, two contrasting mechanisms are considered for the bending of 2D layered nanomaterials: platelike bending, where the layers bend collectively and

do not slide relative to each other, or a mechanism where layer sliding occurs.³⁴ One can identify these mechanisms by simply bending a stack of paper. On one hand, in the platelike case there is an invariant neutral surface, on the opposite sides of which there is extension and compression of the constituent layers. On the other hand, bending accompanied by layer sliding efficiently releases these in-plane strains on both sides of the neutral surface. In our case, the two ends of the SPN were constricted by either the silver glue or the W probe tip. The interlayer sliding could not occur freely. Thus, the bending in the SPN should commence in a platelike manner. This indicates that for the free standing 2D layered atomic crystals, the actual deformation process greatly depends on the boundary conditions. Interestingly, the dark fringe did not move any more in spite of further violent bending by folding up the SFN, as shown in Fig. 6e. Anyway, the SPN did not fracture or break in appearance, and effectively withstood the violent bending distortion. When we retracted the W tip, the bending did not disappear (Fig. 6f). These observations imply that the bending-induced deformations did not spontaneously return to their original shape without the aid of external force.

The *in situ* scrolling behaviour of a SPN was also initiated by manipulating the W tip to contact the flake edge with great care (Fig. 7a). Pushing the edge forward and upward caused the scrolling of the nanoflake marked with red arrow in Fig. 7b. When we retracted the W tip, the scrolled nanoflake did not spontaneously return to its original sheet-like morphology, as shown in Fig. 7c. This is similar to the bending behaviour observed in Fig. 6. Further pushing the nanoflake resulted in multiple scrolling (Fig. 7d). The whole scrolling process can be schematically shown in Fig. 7g. With the aid of Van der Waals' force between the W tip and the nanoflake, we could flatten the scrolled nanoflake (Fig. 7e) by retracting slowly the W tip. No obvious fracturing was visible during the *in situ* scrolling and flattening of the SPN. The flattened flake could be easily scrolled again without any fracturing (Fig. 7f), proving its superior nanomechanical flexibility and reliability. From the bending and scrolling experiments, we find that the bent or scrolled SPNs did not spontaneously return to its original flake-like morphology. This finding indicate that unique puckered structure of black phosphorus could be responsible for extraordinary mechanical properties of the SPNs, which is different from the previous reports of carbon nanotubes,³⁵ graphene and boron nitride nanoribbons,³⁴ where the bending process was spontaneously reversible, with the nanoribbons or nanotubes returning to their pristine morphologies when unloading the applied external force. Interestingly, we did not observe naturally scrolled edges for the suspended SPNs if no external force was introduced, as shown in Fig. 5.

Beside the out-of-plane mechanical behaviours, in-plane stretching behaviour of the individual SPNs was also *in situ* investigated. A pristine SPN with two edges protruding from Cu grid was selected (Fig. 8a). We know that van der Waals' force between the W probe and the SPN cannot be used to stretch the SPN when they contact. This is because that a few atom van der Waals contact is much weaker than the P-P interatomic covalent bondings on the whole SPN where the total number of bondings is considerably larger. Thus, the contact between the W probe and the SPN must be fixed. For this purpose, we first deposited amorphous carbon (a-C) on the W probe via electron-beam-induced a-C deposition,^{36,37} as shown in Fig. 8a. After the contact (Fig. 8b), the second a-C deposition was performed on the contact region and the SPN and the W probe were firmly soldered. Then, *in situ* stretching experiment was carried out along the direction of edge L_1 (Fig. 8b) by retracting the W probe with great care. Concomitant strain fringe contrast immediately occurred upon stretching for the SPN (Fig. 8c). The initial L_1 length was 1.3 μm and was gradually stretched to 1.75 μm (Fig. 8d–f). Note that no terrible fracture or break was observed for the SPN during the whole stretching process. The large strain value of 34% approximates to near the theoretical value of 32% along the armchair direction of multilayered BP.¹⁸ Regrettably, we cannot obtain electron diffraction (ED) to identify the crystallographic direction along the edge L_1 due to the unavoidable deflection of the nanoflake during the dynamic *in situ* experiments. Even so, the large strain is conceivable considering the unique puckered structure of BP. For instance, the tensile strain applied along the armchair direction can effectively flatten the puckers, rather than significantly extending the P-P bond lengths. These compromised dihedral angles significantly reduce the required strain energy, suggesting great applications of large-magnitude-strain engineering. The *in situ* stretching experiment intuitively demonstrated the possibility of large

in-plane tensile strain of the SPNs that can be directly seen real time.

Conclusions

In summary, we have demonstrated that high-quality mono-/few-layer SPNs can be exfoliated in organic solvents using a very simple form of rotating-blade mixer: a household kitchen blender. We find that the surface tensions of the applied solvents greatly affect the size of the SPNs. The average L of the SPNs shows a rising trend with increasing the surface tensions of the solvents, while the L/T ratios rose first and then dropped. CHP, DMAC, and DMF are more suitable for preparing the SPNs with high L/T ratios. More importantly, we for the first time investigated nanomechanical properties of the SPNs by combining *in situ* transmission electron microscopy (TEM) imaging and *in situ* micro-manipulation system to directly visualize the mechanical behaviours of individual phosphorene nanoflakes. The nanoflakes can be easily bent, scrolled, and stretched, showing remarkable out-of-plane and in-plane mechanical flexibility rather than fracturing. This investigation indicates potential applications of the SFNs in flexible nanoelectronic devices in the future.

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Fig. 1 (a) Illustration of the shear-exfoliation process from bulk BP crystals to SPNs dispersion by a household kitchen blender. (b) Illustration of *in situ* TEM experiment for studying mechanical flexibility of the SPNs.

Fig. 2 TEM, SAED, EDS mapping characterization of the SPNs prepared in CHP. (a) A typical TEM image of an ultrathin SPN on a lacy carbon film. Inset shows schematically the atomic structure of monolayer black phosphorus along top-view projection. (b) High-resolution TEM (HRTEM) image and (c) corresponding SAED pattern of the monolayer SPN corresponding to (a). A filtered section of HRTEM image (low-left inset in (b)) is in agreement with the atomic structure characteristic of monolayer phosphorene. (d) A typical STEM-HAADF image of another SPN, revealing its uniformity in thickness. (e, f) EDS mapping of C and P elements corresponding to (d). Comparison between STEM-HAADF image and element mapping images indicates high-purity of the SPNs.

Fig. 3 (a) Low-loss and (b) core-loss EELS of the SPNs prepared in CHP. The characteristic core-loss peak at 133 eV corresponding to the P $L_{2,3}$ edge is observed clearly. (c) Raman spectrum of the SPNs on a SiO_2/Si substrate, showing the characteristic Raman bands at 363 cm^{-1} , 438 cm^{-1} , and 465 cm^{-1} assigned to the A_g^1 , B_{2g} , and A_g^2 photon modes for black phosphorus, respectively.

Fig. 4 SEM and AFM images of the few-layer-thick SPNs prepared in CHP. (a,b) SEM images of the SPNs. (c) AFM height measurement of the SPNs. The height profile corresponds to the drawn white line. Statistical results of (d) average length and (e) average thickness of the SPNs.

Fig. 5 TEM images and corresponding statistical average length and thickness of the SPNs exfoliated in different organic solvents, (a) *N*-methyl-pyrrolidone (NMP), (b) 1,4-dioxane, (c) dimethyl sulfoxide (DMSO), (d) dimethylacetamide (DMA), (e) dimethylformamide (DMF), and (f) isopropanol (IPA). 1,4-dioxane, (c) dimethyl sulfoxide (DMSO), (d) dimethylacetamide (DMA), (e) dimethylformamide (DMF), and (f) isopropanol (IPA). (g) Statistical average length (L), (h) average thickness (T), and (i) the L/T ratios of the SPNs as a function of surface tensions of the solvents.

Fig. 6 Series of TEM images of *in situ* bending process of an individual SPN by using the W probe to bend the SPN.

Fig. 7 Series of TEM images of *in situ* curling and uncurling experiments of an individual SPN. (a) Pristine SPN before curling. (b) SPN curled by push flake edge by moving forward the W tip. (c) The curl still existed after withdrawing the tip with great care. (d–f) Further curling and uncurling processes were repeatable and reversible. (g) A schematic diagram shows the scrolling process of the SPN.

Fig. 8 (a) Before the stretching experiment, amorphous carbon (a-C) was beforehand deposited on the W probe via electron-beam-induced a-C deposition method. (b) After the contact between the SPN and the W probe, a second a-C deposition was performed on the contact region and the SPN and the W probe were firmly soldered. (c–f) Series of TEM images of in-plane *in situ* stretching experiments of the individual SPN.