

A Study on Synthesis and Fabrication Methods of 2D VA Material - Phosphorene

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Abstract - Black phosphorus has emerged as a new, intriguing two-dimensional (2D) material, together with its monolayer, which is referred to as phosphorene. The exploration of this new 2D material demands various synthesis and fabrication methods to achieve potential application. The main focus of this article concerns the various synthesis and fabrication methods of layered phosphorene, which may pave the way towards the realization of high-performance nano-devices.

Key Words: Phosphorene, 2D-Materials, Exfoliation, Sonication

1. INTRODUCTION

Few-layer black phosphorus (phosphorene), as a novel two-dimensional (2D) material, is gaining researchers' attention due to the exceptional properties, including puckered layer structure, widely tunable band gap, strong in-plane anisotropy, and high carrier mobility. Phosphorene application expanded from energy storage and conversion devices to thermoelectrics, optoelectronic and spintronic to sensors and actuators. Black phosphorus (BP) has sparked enormous research interest since its discovery in 2014 due to its distinctive structures and useful properties. Phosphorene has been considered to be a more favourable material on balance than the other 2D layered materials due to its wide range of fascinating properties. In this article we will briefly discuss about the different Synthesis methods & Fabrication methods adopted for Phosphorene.

2. SYNTHESIS OF PHOSPHORENE

The growing interest in phosphorene due to its great potential has increased the demand for large BP crystals for use in industrial applications. BP in its bulk form can be synthesized through different methods such as the High-pressure route, Recrystallization from Bismuth (Bi) flux, Chemical vapor transport and Mechanical milling.

2.1. High-Pressure Route

Bridgman [1] explained the discovery of black phosphorus as an event that occurred when ordinary white phosphorus (white P) was forced to change into red phosphorus (red P) under high hydrostatic pressure. The transition from white to black phosphorus occurred when

pressure ($\approx 11\ 000$ to $13\ 000\ \text{kg cm}^{-2}$) was applied at room temperature to the white phosphorus through a kerosene medium at $200\ ^\circ\text{C}$, in an oil bath controlled by a thermostat. Bulk BP was also produced under a constant pressure of 10 kbar by heating red phosphorus to $1000\ ^\circ\text{C}$ and slow cooling it to $600\ ^\circ\text{C}$ at a cooling rate of $100\ ^\circ\text{C h}^{-1}$ [1]. The high-pressure environment was provided by a cubic-anvil type of apparatus.

Synthesized BP should be kept in an inert atmosphere. A high-temperature high-pressure (HTHP) method was reported for the preparation of BP using a cubic-anvil high-pressure apparatus under a pressure of 2 to 5 GPa, where the blocks of white P and red P powder were shaped into cylindrical capsules (3-mm thick and 10-mm in diameter) in a chamber made of sintered boron nitride [2]. Subsequently, pressure was applied with six tungsten carbide anvils to the cube containing the sample and a heater. The successfully synthesized WBP (black P obtained from white P) under different conditions has a metallic luster and a dark gray color. The synthesized WBP could be easily distinguished from their appearance (metallic luster, dark grey in color). High resolution TEM (HRTEM) confirmed the puckered layer structure with polycrystallinity as seen from the concentric diffraction rings and irregular diffraction spots.

2.2. Recrystallization from Bi Flux

The preparation of needle-shaped BP single crystals from a solution of white P in liquid bismuth, usually called the bismuth-flux method, was reported by Brown and Rundqvist [3] in 1965. From the reports of Iwasaki et al. [64], the needle-shaped BP crystals grown by the Bi-flux method demonstrate a 2D Anderson localization in electrical properties at low temperatures. Baba et al. [4] reported on BP crystals grown in different shapes from a solution of white P in liquid Bi via an improved Bi-flux method, with reduced chemical impurities. It is also very difficult to have highly pure white P due to its chemical activity [4]. The entire process of converting the red P to white P and the crystallization of BP was carried out in an evacuated quartz-glass apparatus inside vacuum because white P should not be exposed to air as it is poisonous, highly reactive and inflammable in air [4]. A quartz ampoule containing the white P (with a melting point of $44.1\ ^\circ\text{C}$) was

melted at 80 °C and then moved towards the Bi (heated to 300 °C). Later, the ampoule was placed in an electric furnace, heated to 400 °C for 48 h and finally cooled down.

2.3. Chemical Vapor Transport

Single crystals of BP can be grown by the chemical vapor transport (CVT) method [5]. The process is detailed as follows: Red Phosphorus, Gold Tin metal (AuSn) and Tin (IV) Iodide (SnI₄) were sealed in an evacuated long quartz ampoule. The charged end of the ampoule was placed horizontally at the center of a single-zone tube furnace. The ampoule was slowly heated to 873 K for 10 h and maintained at the same temperature for 24 h. The ampoule was subsequently cooled to 773 K at a rate of 40 K h⁻¹. BP single crystals were crystallized in the form of flakes at the cold end of the ampoule. The low-pressure route, with the use of a mineralizer as the reaction promoter, was of interest because of its high yield in non-toxic experimental conditions [5]. The red phosphorus, converted to BP by SnI₄ mineralization, gives red phosphorus and Au as its byproducts [6].

Nilges et al. [7] used the mineralizer SnI₄ prepared from tin powder and iodine in 25 mL toluene (starting materials) that was refluxed for 30 min; the synthesis process adopted by them for the low-pressure route is subsequently described. AuSn was synthesized from an equimolar mixture of gold and tin in a sealed evacuated silica ampoule, and AuSn was adopted as a binary precursor to accelerate the reaction of polyphosphide Au₃SnP₇ at elevated temperatures prior to the transport reaction. The starting materials were melted by a H₂/O₂ burner before the growth process. The starting materials of red phosphorus, AuSn and SnI₄ were placed in the silica ampoule (10 cm in length, 10 mm in diameter), which was evacuated to a 10⁻³ mbar pressure and placed in a muffle furnace (873 K, 23 h), resulting in the formation of BP crystals (>1 cm). The Sn to SnI₄ ratio is the most critical factor for the successful growth of high quality BP bulk crystals. The final BP product was collected and washed repeatedly with hot toluene and acetone for an enhanced removal of the residual mineralizer [8]. A modified mineralizer-assisted short-way transport reaction involving red phosphorus, Sn/SnI₄ as the mineralization additive to promote short reaction times, and high-quality large BP crystals was also reported in the literature [9].

2.4. Mechanical Milling

BP can be prepared by a mechanical milling process using a mixer mill and a planetary ball-mill apparatus with red phosphorus powder as the starting material [10]. The process was carried out in a stainless steel pot with 10 stainless steel balls (10 mm or 12.7 mm in diameter) in Ar atmosphere for 1 h. Composites with a composition of BP

and acetylene black (AB) (80 wt% BP, 20 wt% AB) were prepared by a similar milling technique (a mixer mill) for 1 h. The mixer mill apparatus was found to yield black phosphorus with higher crystallinity depending on the difference in the impact of the mechanochemical reaction for two types of ball-mill apparatuses [11]. Sun et al. [12] synthesized BP from red phosphorus by means of a high-energy mechanical milling method in a ball-mill instrument. Red phosphorus was cleaned with 5% sodium hydroxide solution and distilled water for the removal of oxides. A stainless steel vessel containing red phosphorus and different sized stainless steel balls was sealed in an Ar-filled glove box and rotated for 12 h at 400 rpm.

3. FABRICATION METHOD

The higher intralayer strength and weaker interlayer cohesion of phosphorene enables their top-down synthesis by the cleaving of layers from bulk BP [13]. Apart from the dry and wet transfer methods, few-layered BP can also be fabricated by other methods and we will discuss them in detail in this section.

3.1. Dry Transfer Methods: Mechanical Exfoliation

The mechanical exfoliation (ME) technique is widely adopted in the fabrication of BP [14]. Because of its simplicity and ability to produce high-quality materials, this technique was first utilized in the fabrication of graphene, and it is also growing to be more attractive for the synthesis of other 2D materials (much earlier for MoS₂) that are different from their bulk forms [15].

The performance of BP-based devices not only depends on the number of layers but also on the quality of the crystal lattice [16]. Mechanical exfoliation has been of significance in obtaining the highest-quality samples.

3.1.1. First-Principles Calculations on Mechanical Exfoliation

Mu and Si [17] described the sliding processes of bilayer phosphorene by calculating the sliding energies (E_s) using first-principles calculations with density functional theory (DFT) SIESTA code, including the van der Waals (vdW) correction. Bilayer phosphorene is favored to AB stacking due to its minimum E_s ; the energy curve generated is also reasonable when the vdW interaction is taken into account [18].

The exfoliation of the bilayer phosphorene to create a monolayer along the x-direction requires overcoming the maximum energy barrier of approximately 270 meV. In the case of the sliding process along the y-direction, the energy barrier is approximately 110 meV, which is two times smaller in magnitude than that of the x-direction. The important fact is that the minimum energy barrier exists when the sliding is along the diagonal (xy) direction as a

result of the low energy barrier of approximately 60 meV that originates from the puckered structure of BP [19]. To reduce the energy barrier in phosphorus allotropes, the blue phosphorene might be a good with its more planar in-plane configuration [20]. The significance of this is that the interlayer sliding constraints determine the contribution of interlayer Coulomb interactions to the sliding energy profile which in turn results in different sliding pathways. Hence, the optimal pathway is to slide the BP along the diagonal direction.

3.1.2. A Scotch-Tape-Based Mechanical Exfoliation Method

Mechanical exfoliation using scotch-tape has been reported in many studies [21]. The isolation of single-layer phosphorene that can be performed by means of a classical scotch tape (also called as blue Nitto tape)-based mechanical exfoliation is divided into two steps:

- i. Exfoliation of BP layers from bulk BP using scotch tape and Transfer of the exfoliated BP layers onto the substrate (usually SiO₂). The transfer is performed by aligning the desired BP flake to the targeted substrate.

The exfoliation process must be carried out inside a glove box and kept under vacuum. It is then possible to explore the enormous quantities of information obtained to develop a suitable means for the protection of few-layer BP from degradation.

Saito et al. [22] reported that they covered the BP flakes with a resist (ZEP 520 A) immediately after exfoliation. The resist on the substrate was eventually removed by placing the substrate in N-methyl-2-pyrrolidone (NMP) for 40–60 min at 323 K, followed by sprinkling acetone and drowning it in isopropyl alcohol. Luo et al. [148] used 1- μ m-thick poly(vinyl alcohol) (PVA) baked at 70 °C for 5 min, coated the PVA with a 200-nm-thick poly(methyl methacrylate) (PMMA) and baked the resulting stack at 70 °C for 5 min. The exfoliated BP flakes were transferred to the PMMA/PVA stack which was then cleaved off and flipped over to be mounted on a glass plate for further investigation. The flake, together with the PMMA/PVA stack, was transferred to the desired substrate (200-nm-thick free standing SiN). The sample was drenched (for >12 h) in acetone (>70 mL) to remove the PMMA/PVA and then dried with nitrogen). They also suggested that using a large amount of acetone along with a long soaking time is needed for the effective removal of PMMA. No baking or annealing was performed through the entire processing steps to prevent excessive oxidation and also to retain the BP crystallinity. The degradation of BP was also found to be minimized by coating with only PMMA [23]. The approximate time to cover the flake with PMMA after exfoliation (investigation under a microscope) was estimated to be less than 30 min.

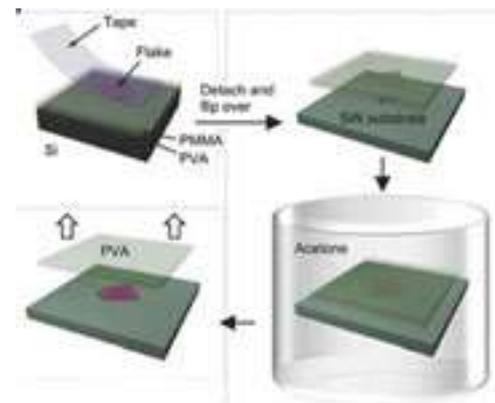


Fig.3.1.2.a. Steps involved in the flake preparation and transfer process. Source [21]

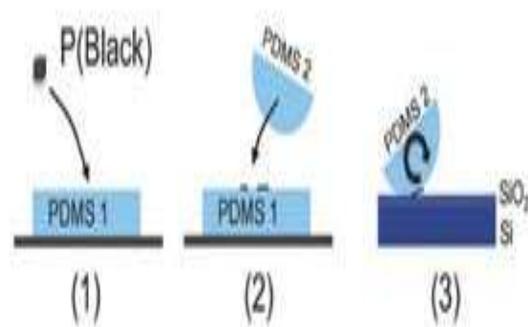


Fig.3.1.2.b. Three-step exfoliation of BP with PDMS. 1) Exfoliation on PDMS-1, 2) Flakes are rolled on the semi-spherical PDMS-2 stamp and 3) The stamp is rolled on the SiO₂/Si substrate. Source [24]

Wang et al. [16] exfoliated BP flakes onto a PDMS stamp on a glass slide. The glass slide is kept in a vacuum chamber ($p \approx 5$ mTorr) immediately after the careful identification of promising flakes for further usage by optical microscopy. The pre-patterned substrate that fits well with the geometry of the chosen flake was used. Wang et al. carried out the transfer by aligning the selected BP flake to the target device area on the substrate. The slide was then lowered to make contact between the PDMS and the substrate. The PDMS was later peeled carefully, leaving BP on the substrate because of the van der Waals forces existing between BP and the surface. This efficient dry transfer method was $\approx 70\%$ successful in the fabrication of good-quality suspended BP nanoelectromechanical systems (NEMS) with sophisticated structures. These wet transfer techniques involve the exposure of BP flakes to wet chemical processes, causing undesired chemical reactions and prolonged time in the ambient condition that leads to unwanted oxidation.

Favron et al. [25] performed the exfoliation of BP in the dark or inside a nitrogen-filled glove box to protect it

from degradation. A SiO₂/Si substrate was coated with 20 nm of parylene C to minimize the influence of hydrophilicity on the surface. The presence of parylene is used for a clear identification of the exfoliated flakes and also as a protection against degradation [24]. The samples can also be washed with acetone, methanol and isopropanol (approximately 1 minute for each step) so that the residue from the scotch tape can be removed; this is followed by baking at 180 °C for 5 min to remove the remaining solvent [26]. A mechanically exfoliated monolayer BP flake was finally obtained.

3.1.3. Modified Mechanical Exfoliation Technique

Modified mechanical exfoliation was introduced by Castellanos-Gomez et al. [27] to optimize the deposition of atomically thin BP flakes. By using an intermediate viscoelastic surface in exfoliation, which increases the yield and further reduces the contamination of exfoliated flakes. Commercially available bulk BP was cleaved multiple times by blue Nitto tape. Later, the tape containing thin BP crystallites was slightly pressed against a polydimethylsiloxane (PDMS)-based substrate and peeled off rapidly. Finally, the thin flakes present on the surface of the PDMS substrate were moved to the desired substrates by simply putting the PDMS substrate in gentle contact with the new acceptor substrate and peeling it off slowly (approximately 5–10 minutes to peel off the stamp completely from the surface). Island et al. reported that long-term exposure to ambient conditions results in a layer-by-layer etching process of BP flakes, which they were able to etch down to a single-layer (phosphorene) thickness (≈ 0.7 nm).

Another modified Scotch-tape exfoliation technique was reported in the literature where BP was first exfoliated onto a flat PDMS stamp and then transferred onto a curved PDMS stamp [28]. Later, the curved PDMS stamp covered with flakes is rolled onto the desired substrate. BP films were also produced by the micromechanical cleavage of bulk BP crystals directly onto a PDMS stamp [27]. As a result of the viscoelastic properties of PDMS, the BP film adheres to the fiber end when the film is gently lifted up from the PDMS stamp [28].

3.2. Wet Transfer Methods: Liquid-Phase Exfoliation

Liquid exfoliation or liquid phase exfoliation (LPE) can be broadly classified into the following basic categories of

- (i) Theoretical Studies of Liquid Exfoliation Of Phosphorene
- (ii) Ion intercalation,
- (iii) Ion exchange,
- (iv) Ultrasonication-assisted exfoliation and
- (v) Shear exfoliation.

In the LPE method, one can achieve large quantities of dispersed nanosheets of layered materials which are more suitable for industrial-scale applications. An earlier study reported in inorganic layered compounds showed the exfoliation of vermiculite clay in liquids via ion intercalation and shear mixing [30]. A few studies were later demonstrated on the use of ultrasonic agitators for ion intercalation-assisted exfoliation of TaS₂, NbS₂, MoS₂ and layered oxides [31]. The LPE method is selective to the dispersion liquid and hence, different solvent have different dispersibility and are found to have diverse nonlinear properties [32].

The primary approach in liquid exfoliation is the oxidation first demonstrated in graphite. This is regarded as one of the oldest methods of exfoliating layered crystals with a low reducing potential followed by subsequent dispersion into suitable solvents [33]. The amount and the type of oxides attached can be changed by means of oxidation to tune the properties such as electrical conductivity and luminescence [34].

3.2.1. Theoretical Studies of Liquid Exfoliation of Phosphorene

The surface energies of the solvent and layered materials play a crucial role in tuning the exfoliation efficiency of the liquid-exfoliation process. The surface energy of bilayer phosphorene was estimated to be ≈ 58.6 mJ m⁻² based on a barrier energy of 60 meV, which fits well in the range of surface energies of solvents such as ethanol (22.0 mJ m⁻²), methanol (41.4 mJ m⁻²), water (72.7 mJ m⁻²) and formamide (57 mJ m⁻²) [55]. This theoretical study supports the thinking that BP can be easily exfoliated by LPE. Sresht et al. [73] studied the LPE of phosphorene in the solvents dimethyl sulfoxide (DMSO), dimethylformamide (DMF), isopropyl alcohol (IPA), NMP and N-cyclohexyl-2-pyrrolidone (CHP) using three molecular-scale computer experiments to model the solvent-phosphorene interactions via atomistic force fields assisted by ab initio calculations and lattice dynamics. The energy needed to peel a single phosphorene monolayer from a stack of BP was measured, with a detailed explanation of the role of the wedges present in solvent molecules for initiating the exfoliation. The main findings of their simulations are given as follows: (1) The lower value of the primary minimum in CHP than the corresponding minimum for vacuum accounts for the easier aggregation of phosphorene monolayers in CHP than in vacuum; this indicates that CHP is a poor choice for LPE and agrees well with experimental results [35], (2) The cohesive strength of IPA is attributed to the hydrogen bonding networks between confined molecules [35], (3) The large energy barrier in DMF is due to (a) the small size and planarity of the DMF molecule giving rise to an enhanced intercalation ability and (b) the substantial cohesive energy that causes the high density, viscosity and boiling point, (4) DMSO, with

its enhanced packing along with its high cohesive energy, high boiling point, density and viscosity, gives the optimal dispersion environment as supported by previous works[35], and (5) The strong cohesive dipolar forces in certain solvents (DMSO, IPA) increase their suitability as stable dispersion media and therefore, solvent planarity improves the dispersion stability and leads to a greater degree of confinement of the solvent molecules between the 2D BP sheets.

The performance of a solvent based on the shape of its molecules in interfacial layers with phosphorene was clearly demonstrated by Sresht et al. [13] In general, LPE starts by the penetration of a wedge of solvent molecules in the interlayer gap of 2D materials. Consequently, the solvents with planar molecules near the phosphorene surface (NMP, DMSO) act as molecular wedges for efficient intercalation [13]. The intercalation can be successful if and only if the new phosphorene surfaces established by the solvent wedge are sustained by sorption forces that exist between the solvent molecules and the corresponding 2D material. Moreover, the cohesive energy density of the solvent molecules in the final interfacial layer of solvent, confined between the sheets, is high and continues to diminish if strong sorptive interactions exist between the confined molecules and the sheets, which favors the stable dispersion of phosphorene. The simulation studies showed that the phosphorene exfoliation is easier if the adhesion between the phosphorene and solvent is stronger than the cohesion between the solvent molecules [13]. Accordingly, the solvent's molecular shape is more important and has to be taken into account in LPE.

3.2.2. Intercalation

Intercalation is a broadly adopted method in liquid exfoliation as the layered materials can adsorb guest molecules in the spacing existing between their layers, thereby forming inclusion complexes [36]. The intercalation process increases the layer spacing, weakens the interlayer adhesion and reduces the energy barrier to exfoliation [33]. The role of the intercalants, such as n-butyllithium and IBr, is to transfer charge to the layers and subsequently decrease the interlayer binding. The exfoliation process is completed with the aid of further thermal shock treatments or ultrasonication [36] in a liquid. The final step is to stabilize the exfoliated flakes either by incorporating a surface charge or by adding surfactant [63]. Although the intercalation techniques are sensitive to ambient conditions, they yield a large quantity of the exfoliated nanosheets [36].

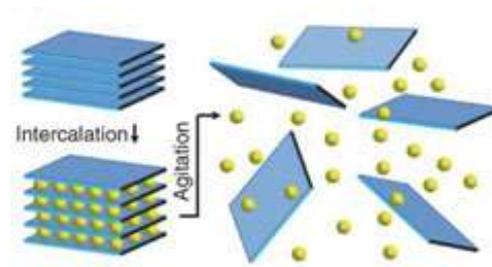


Fig.3.2.2. Ion intercalation: Ions (yellow spheres) are intercalated between the layers in the liquid, swelling the crystal and weakening the interlayer attraction. Shear, ultrasonication or thermal agitation can completely separate the layers, thus producing the final exfoliated dispersion. Source [33]

3.2.3. Ion-exchange

Ion-exchange methods make use of the exchangeable interlayer of cationic counterions present in clays and metal oxides [37]. The most recent approach in liquid-phase exfoliation was performed by ultrasonication in a solvent by exposing the 2D materials to ultrasonic waves that develop cavitation bubbles and collapse into high-energy jets to cleave the layered crystallites, leading to exfoliation [5]. It was demonstrated that the energy difference between the exfoliated and re-aggregated flakes depends on the surface energy of the solvent and may be small if both the solvent and 2D material have the same surface energy [38]. By ultrasonication with organic solvents and ionic liquids, shear exfoliation methods have been widely utilized in the liquid exfoliation of BP. Interestingly, there is a correlation between the cohesive energy of a 2D material and the solvent used that determines the capability of a particular solvent to achieve efficient exfoliation and create a stable dispersion [39]. The cohesive energies can be evaluated by using two significant parameters: (a) The Hildebrand solubility parameter and (b) The Hansen solubility parameter. The Hildebrand solubility parameter is the measure of a solvent's total cohesive energy per unit volume and the Hansen solubility parameter is the measure of the dispersive, polar and hydrogen bonding components of a solvent's cohesive energy per unit volume [40]. If the Hansen solubility parameters of the desired 2D material and solvent are the same, that solvent would be the best candidate for exfoliation.

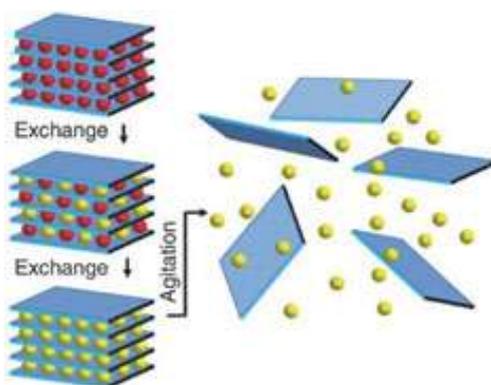


Fig.3.2.3. Ion exchange: Ions found between the layers in layered materials balance the surface charge on the layers. These ions (red spheres) can be interchanged in the liquid for other larger ions (yellow spheres), and further agitation yields the exfoliated dispersion. Source [33]

3.2.4. Ultrasonication-Based Exfoliation

Different approaches were adopted in the ultrasonication of 2D materials including organic solvent-based exfoliation, stabilizer-based exfoliation, ionic liquid-based exfoliation, salt-assisted exfoliation, intercalant-assisted exfoliation and ion exchange-based exfoliation [40]. Ultrasonication can be performed either by the bath sonication or the tip sonication technique. Bath sonication is used in majority of studies and hence, we do not mention it specifically and the general term of ultrasonication is used to denote “Bath Sonication” throughout this article.

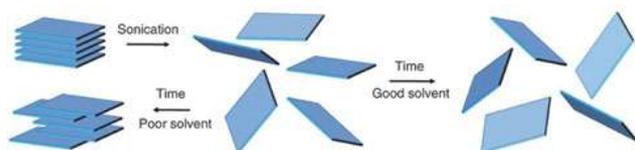


Fig.3.2.4. Sonication assisted exfoliation: The layered material is sonicated in a solvent to form a nanosheet by means of exfoliation. In the case of a good solvent with an appropriate surface energy, stabilized nanosheets are formed; bad solvents cause reaggregation leading to sedimentation. Source [33]

3.2.4.1. Organic-Solvent-Based Sonication

One of the approaches used involved BP crystals mixed with ethanol solution and ultrasonicated (400 W) at room temperature (RT) for 43 h. The resulting solution was centrifuged (at 4000 rpm for 60 min) to eliminate larger particles and led to a final purified BP-ethanol mixture (with a concentration of $\approx 6 \text{ mg mL}^{-1}$) [41]. It was also reported that BP powder was obtained by grinding bulk BP crystal dispersed in different solvents such as IPA, NMP and ethyl alcohol (EA) to obtain 1 mg mL^{-1} dispersions, and the dispersions were ultrasonicated for 2 h. The dispersions

were then allowed to settle for more than 24 h to enable the removal of large-size sedimentations by centrifugation (at 1500 rpm for 20 min). The formation of thin BP nanoflakes in the solution is that the interlayer van der Waals bonding is broken down by the ultrasonic energy [42].

Guo et al. [43] reported a basic NMP-based LPE method for the fabrication of phosphorene with an excellent water stability, a controllable size, a number of layers and high yield. The schematic of the synthesis process of basic NMP-exfoliated phosphorene is given in Figure 3.2.4.1.b. The basic NMP-exfoliation process can be detailed as follows: bulk BP (15 mg) was added to a saturated NaOH NMP solution (30 mL) and sonicated for 4 hours at 40 kHz frequency and 80% power, and the phosphorene in NMP was separated and transferred to water by centrifugation (at 3000 rpm for 10 min) in order to remove the unexfoliated bulk BP. Guo et al. [43] adopted different centrifugation speeds to control the phosphorene thickness. The supernatant solution was centrifuged at 12 000 rpm for 20 min to obtain $5.3 \pm 2.0 \text{ nm}$ thick (5 to 12 L) phosphorene samples with an average diameter of $\approx 670 \text{ nm}$ (referred to as 12000 phosphorene) and further centrifuged at 18 000 rpm for 20 min to obtain $2.8 \pm 1.5 \text{ nm}$ thick (1 to 7 L) phosphorene samples with average diameter of $\approx 210 \text{ nm}$ (referred to as 18000 phosphorene). The results are also demonstrated for the two conditions with and without the addition of NaOH to NMP, which confirms that a thorough exfoliation of BP was achieved by the basic NMP process (with NaOH) than by the NMP-only exfoliation (without NaOH). The negative charge of phosphorene corresponds to the OH^- ions, obtained by adding NaOH, that are absorbed on the surface of phosphorene leading to an excellent stability in water.

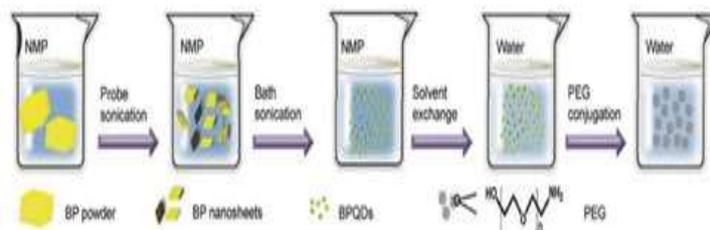


Fig.3.2.4.1.a. Steps followed in the fabrication and surface modification of BP QDs. Source [43]

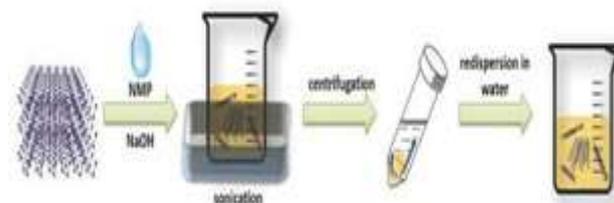


Fig.3.2.4.1.b. Schematic of synthesis process of basic NMP- exfoliated phosphorene. Source [43]

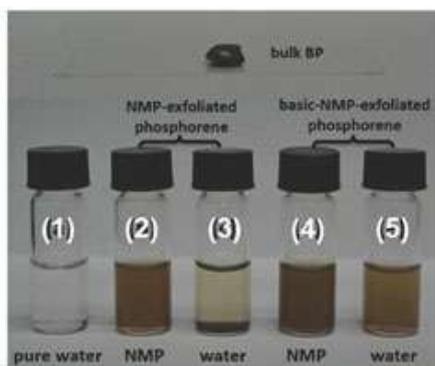


Fig.3.2.4.1.c. Phosphorene dispersed in NMP and water. The five bottles contain the following: 1) Pure water, 2) NMP-exfoliated phosphorene in NMP, 3) NMP-exfoliated phosphorene in water, 4) Basic NMP-exfoliated phosphorene in NMP, and 5) Basic NMP-exfoliated phosphorene in water. Source [43]

Zhang et al. [2] synthesized BP quantum dots (QDs), with an average size of 1.9 to 4.9 nm and excellent stability in NMP, using ice-bath sonication (3 h, 200 W). The BP (5 mg) and NMP (1mL) ingredients were grinded in a mortar for 20 min, transferred to a glass vial with 3 mL of NMP and sonicated for 3 h.

Yasaei et al. [35] examined various solvents from different chemical families such as alcohols, chloro-organic solvents, ketones, cyclic or aliphatic pyrrolidones, N-alkyl-substituted amides and organosulfur compounds, which encompass a wide range of surface tensions (21.7 to 42.78 dyne cm^{-1}) and polar interaction parameters (2.98 to 9.3 $\text{MPa}^{1/2}$) to understand their performance in BP exfoliation. The bulk BP crystal (0.02 mg in 10 mL) was immersed in different solvents for a 15 h sonication (130 W, a total input energy of 1 MJ) and they found that aprotic and polar solvents such as DMF and DMSO as more suitable for atomically thin BP flakes, leaving stable and uniform dispersions[44]. A 30 min centrifugation was performed at 2000 rpm, after which the supernatants with concentrations of up to 10 $\mu\text{g mL}^{-1}$ were collected and dispersed in IPA. The dispersed flakes in the solution offer the best protection from degradation.

Woomer et al. [45] surveyed the experimental conditions for liquid exfoliation and explored the first large-scale production (10 g scale) of monolayer, bilayer and few-layer phosphorus. The experimental process is described as follows: Grounded BP was sonicated in anhydrous, deoxygenated organic liquids (isopropanol for 16 h) under inert atmosphere resulting in a change of color from black to reddish-brown and finally to yellow that signifies a change in the electronic structure of BP. The color remains the same after few weeks with limited reaggregation, indicating the presence of small phosphorus particulates.

3.2.4.2. Water-Based Sonication

Wang et al. [8] used distilled water as the solvent, and it was bubbled with argon to eliminate the dissolved oxygen molecules to overcome the problem of oxidation in the sonication process. A scalable clean exfoliation with water of few-layer BP was recently demonstrated by means of the tip sonication method [46]. Bulk BP crystals were grounded to BP powders, the powders were dispersed in 20 mL of deionized (DI) water to obtain a concentration of 1 to 10 mg mL^{-1} , and the dispersions were tip sonicated for 30 to 300 min. The supernatant was decanted from the settled dispersion after 12 h for centrifugation, yielding a BP nanosheet dispersion with a high concentration. The interesting finding of this study is that the BP nanosheets retain the high quality of the bulk crystals, with the excellent qualities of a very high crystallinity, an impurity-free structure and stability in water. Lee et al.[62] prepared few-nm to <20 nm BP nanodots with an average diameter of ≈ 10 nm and a height of ≈ 8.7 nm, where BP (0.4 g, 12.8 mmol) was dispersed in distilled water (100 mL) for a 30 min sonication (20 kHz, 100 W). The supernatant liquid collected from the dispersion was ultrasonicated for 10 min and these steps were repeated two or more times to create smaller-sized BP particles.

3.2.4.3. Ionic-Liquid-Based Sonication

Ionic liquids (ILs) are molten salts at RT that have been considered as green solvents for decades,[47] with exciting properties such as non-volatility, high thermal stability, high viscosity, high ionic conductivity, nontoxicity, versatile solubility and solvent recyclability compared to conventional organic solvents[48]. ILs are presented by researchers for efficient exfoliation of 2D materials to obtain a stable yield with a high concentration of the suspended nanoflakes [49] ILs exhibit viscosities that are 1–3 orders of magnitude more than those of conventional organic solvents; this influences the rate of mass transport within the solution by preventing the BP nanosheets from restacking [50]. An environmentally friendly liquid exfoliation by means of ionic liquids was reported by Zhao et al. [50] to exfoliate highly pure, crystalline, atomic-scale and uniform mono- to few-layer BP nanosheets by mild grinding and weak sonication. The first step in IL-exfoliation was grinding bulk BP (30 mg) with ILs (0.5 mL) for 20 min using an agate mortar with a pestle that supplements the mechanical shear forces to reduce the exfoliation time due to the increase in the surface area of BP [49]. The next step was to disperse the mixtures in ILs (3 mg mL^{-1} BP) by ice-bath sonication (100 W) for 24 h to obtain suspensions of BP flakes which were further centrifuged at 4000 rpm for 45 min to remove the unexfoliated BP. The stable dispersions of BP nanosheets were obtained, with higher concentrations (≈ 0.95 mg mL^{-1}) than the concentration (0.4 mg mL^{-1}) obtained in NMP, and without sedimentation and aggregation [51]. ILs with larger surface tensions yield

higher-concentration dispersions as a result of the easy break down in the interlayer van der Waals forces of bulk BP by the large surface tension, thereby preventing detached BP layers from restacking [52]. Hence, ILs are found to be more suitable solvents for the fabrication of atomically thin BP nanoflakes due to their strong cohesive dipolar nature and the planarity of the solvents.

3.2.4.4. Tip-Sonication-Based Exfoliation

Kang et al. [51] synthesized electronic-grade BP dispersions using sealed-tip ultrasonication at a reduced sonication time by means of anhydrous oxygen-free organic solvents, thus avoiding the chemical degradation pathways for BP. A sealed container lid was attached to an ultrasonicator tip/probe (0.125 in.) and driven at a higher power compared to conventional bath sonication to minimize the ultrasonication duration. Additionally, the interface between the tip and the lid was carefully sealed with PDMS, whereas Parafilm and Teflon tapes were used to seal the pathways between the lid and container to restrict O₂ and H₂O penetration. The synthesis was performed in an ice bath at ≈ 30 W power to obtain a BP concentration of ≈ 1 mg mL⁻¹ in 1 h; on the other hand, bath sonication needs 15 to 24 h for the same exfoliation process [53]. To optimize the solvent, BP crystals were ultrasonicated under identical preparation conditions in acetone, chloroform, hexane, ethanol, IPA, DMF, and NMP, and the samples were opened only in an Ar glovebox to minimize O₂ and H₂O contamination. The obtained dispersions were further centrifuged at different speeds (500 to 15000 rpm) for 10 min to tune the size distribution of the solvent-exfoliated BP nanosheets, resulting in the solution color changing from brown to yellow depending on the centrifugation speed (see Fig. 3.2.4.4.). They confirmed a monotonic increase in the BP concentration with an increase in boiling point and surface tension; which agrees well with graphene [61]. According to their results, NMP was found to be the optimal solvent to achieve stable BP dispersions. The light yellow solution has the most dilute concentration (≈ 0.01 mg mL⁻¹) of BP nanosheets, which confirms the correlation between the centrifugation speed and the BP concentration. Moreover, the flake thickness and lateral size were also observed to decrease with increasing centrifugation speeds, and the BP dispersions centrifuged at 500 rpm yield thick BP nanosheets (>50 nm thick). Conversely, centrifugation speeds of 10000 and 15000 rpm minimize the lateral size of the BP nanosheet in comparison with the BP dispersions centrifuged at 5000 rpm, giving rise to a relatively lower lateral area for the higher centrifugation speeds. Although probe sonication and bath sonication are commonly used in the exfoliation of 2D layered materials, bath sonication was reported to be more efficient than probe sonication and the use of either one of them may result in the formation of irregular BP nanosheets [53]. Therefore, highly dispersed suspensions of ultrasmall BP QDs with a lateral size of 2.6 nm and a thickness of ≈ 1.5

nm were fabricated by the LPE technique using probe sonication and bath sonication in NMP [117]. Bulk BP crystals were used directly as the starting material without any prior grinding. BP (25 mg) added to NMP (25 mL) was first tip sonicated (1200 W power) for 3 h. The collected dispersion was ice-bath sonicated (300 W) continuously for 10 h. The dispersion was centrifuged at 7000 rpm for 20 min and the collected supernatant solution with BP QDs was further centrifuged at 12 000 rpm for 20 min. The BP QDs were dispersed in water, after centrifugation, and polyethylene glycol (PEG) was conjugated to them to enhance their stability [54].

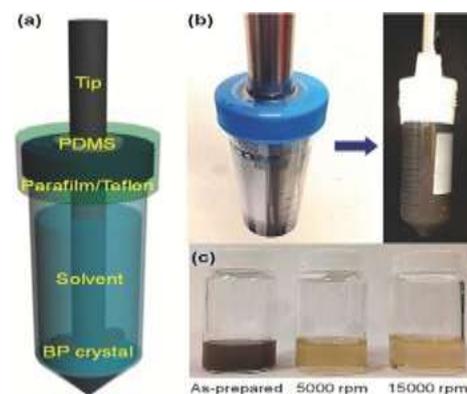


Fig.3.2.4.4. Tip ultrasonication exfoliation of BP in various solvents: Schematic (a) and photo with minimized exposure to ambient air (b) of the experimental setup. (c) Photo of an ultrasonicated BP dispersion in NMP, 5000 rpm centrifugation and 15 000 rpm centrifugation (from left to right). Source [51]

3.2.4.5. Ultrasonication Mediated by Mechanical Milling

Sofer et al. [55] ground bulk BP crystals in an agate mortar (10 min), ultrasonicated in DMF, NMP bis(2-methoxyethyl) ether (DIGLYM) and acetonitrile (AN), and then milled at different times (up to 6 h) and milling speeds. The resultant BP nanoparticles (NPs) were separated by centrifugation and the average size of the colloidal particles (80–200 nm) depended on the milling speed, time and solvent. The solvent used significantly influenced the yield of the milling procedure, reaching 33 wt% for DIGLYM, 36 wt% for DMF, 47 wt% for NMP and 66 wt% for AN. Although AN gave the highest yield of BP nanoparticles, the long term stability of the BP nanoparticles produced was limited. This could be improved by transferring the BP nanoparticles from AN to DMF to form a stable colloidal solution [55]. The removal of larger particles and the improvement of the particle size distribution was attained by centrifugation (at 5000 rpm and 10 000 rpm). The smallest BP quantum dots were obtained in AN and DMF at a centrifugation speed of 10 000 rpm.

3.2.5. Shear-Assisted Exfoliation

Shear-assisted exfoliation is one of the LPE techniques adopted in the exfoliation of 2D materials. Woomer et al. [45] exfoliated large-scale BP (10 g) by a shear mixing process using a shear mixer with square holes at RT, and in oxygen-free and water-free conditions, by bubbling nitrogen gas into the mixing container. They used two different types of BP (crystalline and polycrystalline) and NMP (specific grade) [56] as the solvent. The high-quality crystalline BP with millimeter-sized crystals was difficult to grind but the low-quality polycrystalline BP with trace amounts of red phosphorus was easy to grind. The low-quality material could be successfully exfoliated by shear mixing irrespective of the conditions of shear mixing and the grade of NMP. Specifically, the separation of the layers is nucleated at the grain boundaries or at other defects in the material. High-quality pulverized BP (6 g) was mixed with NMP (100 mL) and bath sonicated for 2 h. NMP (700 mL) was added to the sample and shear mixing was performed at 5000 rpm for 4 h. The dispersion was sonicated again for 3 h, shear mixed at 5000 rpm for 1 h and centrifuged. It was reported that 25% of the samples obtained by the large-scale shear mixing process were monolayers with a lateral size comparable to that produced by small-scale bath sonication [45]. Fig.3.2.5.a shows details of the scaled production method, with photographs of the exfoliated solutions from 6 g of BP and 800 mL of NMP used to yield a highly concentrated suspension with thin pieces by centrifuging 40 mL of the above-mentioned mixture at 20200 g. The size distribution is also shown.

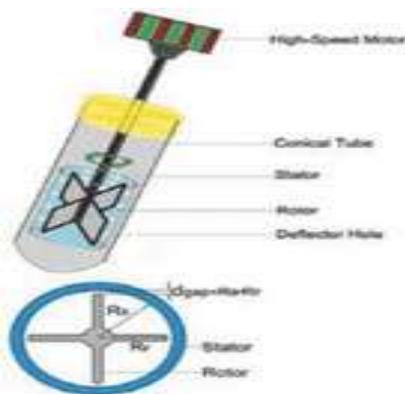


Fig.3.2.5.a Schematic of experimental setup for exfoliating bulk BP. Source [57]

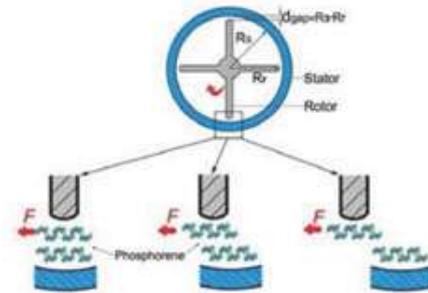


Fig.3.2.5.b Schematic of shear-exfoliation in the laminar flow regime. Source [57]

Xu et al. [57] demonstrated a shear exfoliation technique by making use of shear force to break down the interlayer van der Waals forces in appropriate solvents for exfoliation of monolayer or few-layer phosphorene nanoflakes. A schematic of the experimental setup for exfoliating bulk BP, a schematic of shear-exfoliation in the laminar flow regime, and AFM and SEM images of the exfoliated flakes are shown in Fig.3.2.5.b. The shear-exfoliation process was carried out in an argon atmosphere with the BP immersed in NMP placed in a conical tube inside a glove box. The glove box contained a mixing head with a narrow gap ($d = 0.2 \text{ mm}$) between the rotor and stator in which the high speed of rotor (N) caused a high shear rate (γ) within the gap. The turbid dispersion, obtained from shear exfoliation with a predetermined time and rotation speed, was purified by centrifugation for the removal of larger unexfoliated BP crystal lumps. The different centrifugation speeds produced phosphorene dispersions that were brown to pale yellow in colour. Consequently, the dispersions were filtered using a polytetrafluoroethylene (PTFE) membrane and were rinsed thoroughly with IPA for further removal of the NMP residual. The shear rate is a crucial parameter in shear exfoliation.

The equation of shear rate can be given as [57]:

$$\gamma \approx \pi N(2R_r)/d_{\text{gap}}$$

where N , R_r , d_{gap} are the rotor speed, rotor radius, and rotor-stator gap, respectively. The shear rate increases proportionally with the rotor speed if the mixing head of the rotor-stator is fixed ($R_r = 16 \text{ nm}$, $d_{\text{gap}} = 0.2 \text{ mm}$). The rotor speed (above a minimum of $\approx 1500 \text{ rpm}$) yields high-quality phosphorene nanoflakes with a minimum shear rate of $\approx 1.25 \times 10^4 \text{ s}^{-1}$. The Reynolds number (Re) can be expressed as:

$$Re \approx N(2R_r)^2(\rho/\eta)$$

where ρ and η are the volume and viscosity of the NMP solvent, respectively; the minimum shear rate can be obtained within the laminar flow regime ($Re < 10^4$) [120]. Phosphorene nanoflakes were successfully produced by a Jiuyang kitchen blender with rotating blades (rotation speed of $\approx 15\,500 - 22\,000$ rpm), resulting in a fully developed turbulence ($Re > 10^4$) [57].

3.3. Other Methods

Other methods used for fabrication of 2D material Phosphorene are Plasma-Assisted Fabrication and Pulsed Laser Deposition Amorphous.

3.3.1. Plasma-Assisted Fabrication

Layer-by-layer thinning of multilayers of 2D materials under plasma or laser irradiation is an emerging approach for obtaining 2D monolayers [58]. The few-layer phosphorene realized with mechanical cleavage was transferred to a Si substrate coated with a SiO₂ capping layer (300 nm); the film was further thinned down to phosphorene using an Ar⁺ plasma source (power of 30 W) at a pressure of 30 Pa for 20 s at RT.

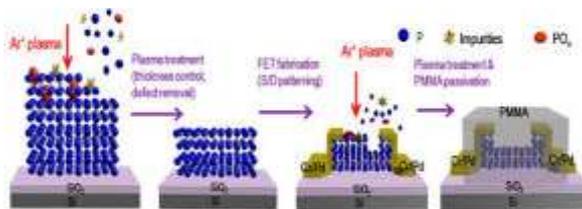


Fig.3.3.1. Plasma etching assisted fabrication: The effects of the plasma treatment on the BP flake: thickness control, surface defect removal and device fabrication. Source [59]

Jia et al. [59] adopted a plasma-etching treatment not only to control the thickness of BP flakes but also to remove the chemical degradation caused on exposed oxidized BP surfaces. The thickness control of few-layer BP was tuned by the plasma etching time. Fig.3.3.1 explains the illustration of the effects of plasma treatment on a BP flake: There was a uniform decrease (≈ 6 nm) in the BP thickness after the plasma etching process (for 4 min).

3.3.2. Pulsed Laser Deposition Amorphous

BP (a-BP), a highly disordered form with a strong resemblance to BP and a thickness of 2 to 10 nm, was realized using conventional pulsed laser deposition (PLD) at a temperature as low as 150 °C, in contrast to the high-temperature and high-pressure growth techniques [60]. The distance between the target of the bulk BP crystal and the substrates was maintained at 4 cm. The growth chamber was evacuated to a pressure of $\approx 1.5 \times 10^{-7}$ Torr before proceeding to the PLD process. The BP target was ablated by a KrF pulsed laser ($\lambda = 248$ nm) with a 5-Hz

repetition rate and the substrate temperature was kept at 150 °C. To obtain uniform a-BP film growth, the BP target and the substrates were rotated during the deposition. Finally, the system containing the as-deposited a-BP ultra films was cooled down naturally to RT in the presence of high vacuum.

3. CONCLUSION

The present need in device fabrication of phosphorene is the large-scale synthesis, accompanied by the large area growth and the control of the layer thickness. The study of BP towards device fabrication becomes more challenging because of its fast degradation when exposed to ambient conditions. Although significant achievements have been made in the preparation of phosphorene, a synthesis method that is low cost, facile and can efficiently control the number of phosphorene layer is still required.

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