Safe and Fast Synthesis of Black Phosphorus and Its Purification

Shunya Kitada, Natsuhiko Shimizu, and Md Zakir Hossain*

1. INTRODUCTION
Following the mechanical exfoliation of graphene from graphite, investigation of other two-dimensional materials has rapidly increased. To date, the existence of hundreds of 2D materials such as hexagonal boron nitride and transition metal dichalcogenides has been reported. Because of their flat structure and unique electronic and optoelectronic properties, 2D materials appear as materials for next-generation technology. Among the 2D materials, a thin layer of black phosphorus (BP) called phosphorene is a promising material for utilization in several devices because of its tunable direct band gap depending on the number of layers, high carrier mobility, and strong in-plane anisotropy. Although BP is the most stable among the three allotropes of elemental P, it is the most expensive because of difficulties in its synthesis. Indeed, one of the key challenges in materialization of the enormous opportunity for various applications is the quick and cost-effective bulk synthesis of pure BP.

Among the synthetic procedures, high-pressure heating of white or red P, bismuth flux, mercury catalysis, and transport reaction methods are prominent. For an easy and cost-effective synthesis of BP, the chemical transport reaction (CTR) method has become popular. In CTR, red P, Sn, and SnI4 in a definite ratio are loaded into a vacuum-sealed glass ampule (hereafter, glass ampule) and heated to a high temperature for a prolonged period followed by steady cooling of the glass ampule. The minimum time required to synthesize BP by CTR is reported approximately 20 h to 10 days. The X-ray photoelectron spectroscopy (XPS) analysis of the as-prepared BP reveals the presence of Sn and I impurities. During the prolonged heating of red P in the glass ampule, the high pressure of gaseous P formed in the ampule can cause an explosion of the ampule with the evolution of fumes and the spread of tiny fragments of glass. The explosion can cause significant physical injury if appropriate protection gear is not used. Furthermore, exceeding the loading capacity of the glass ampule and improper sealing of the ampule can cause an explosion.

Herein, we report a safe and rapid synthesis procedure for BP devoid of compromising the quality and the reaction yield, and a simple physical and chemical method for cleaning the BP crystals obtained by CTR. We found that the possible danger from the explosions can be prevented by enclosing the glass ampule in a flange-fitted stainless-steel tube without compromising the yield and the quality of BP. In contrast to prolonged heating at approximately 823 K, the BP crystals can be synthesized by immediately cooling (100 K/h) to 400 K after heating the glass ampule to the desired highest temperature (823–873 K) over 2 h. The minimum time required for BP synthesis is estimated to be approximately 5 h. The as-prepared BP predominantly contains Sn and I impurities on the upper layers of the BP flakes. These impurities can be removed by exfoliating the upper layers of the flakes or by combining vacuum annealing at ~600 K and HCl treatment.

Received: January 29, 2020
Accepted: April 30, 2020
Published: May 12, 2020
2. RESULTS AND DISCUSSION

In a typical synthesis of BP by the CTR method, red P, Sn, and SnI₄ are loaded into a vacuum-sealed glass ampule in a definite ratio. Thereafter, the glass ampule is slowly heated (∼150 K/h) to 873 K and maintained for approximately 20 h, followed by a steady cooling to room temperature. Occasionally, the glass ampule explodes and releases heavy fumes into air during heating to 873 K or maintaining the glass ampule at 873 K. To optimize the safe synthesis of BP, glass ampules of varying diameters, lengths, and thicknesses were loaded with different ratios of the reactants. A schematic image of a glass ampule is shown in Table 1, where x and y are the length and the inner diameter of the ampule, respectively, and d is the thickness of the glass ampule. Furthermore, V is the volume calculated from x and y, and the maximum pressure is calculated using the ideal gas equation under the assumption that P is in the atomic state.

The vacuum-sealed glass ampule was then placed into a flange-fitted stainless-steel tube, as shown in Figure 1, and heated in a muffle furnace to ∼873 K. The variations in the dimensions (length x, diameter y, and thickness d) of the glass ampules and ratios of the reactants are shown in Table 1. The successful and unsuccessful events of BP crystal growth are indicated as “synthesized” and “exploded”, respectively, in Table 1. We observed several glass ampule explosions during the synthesis of BP by the CRT method. However, in contrast to big explosions with the release of heavy fumes into air, a mild bomb sound was heard with no fumes in the case of glass ampules enclosed in a flange-fitted stainless-steel tube. Therefore, carrying out the synthesis of BP by enclosing the glass ampule in a flange-fitted stainless-steel tube is safer. Note that the possibility of explosion of the stainless-steel tube is determined by the screw used for closing the tube with the flange. Indeed, the high pressure developed inside the stainless-steel tube owing to the explosion of the glass ampule is rapidly defused because the flange-fitted stainless-steel tube is not air-sealed, that is, no metal or rubber gasket is used to close the tube.

It is expected that the breaking of a glass ampule induced by the internal pressure developed by the P gas should be determined by the diameter and the thickness of the ampule. However, from Table 1, we can observe that although the synthesis of BP was successful at 14 MPa using an ampule of 0.85 cm diameter and 0.075 cm thickness, the glass ampule exploded at 12 MPa. Hence, from Table 1 and other data on successful and unsuccessful events, it is unfeasible to set a critical parameter relative to the internal pressure and the glass ampule dimension (diameter and thickness) for the safe synthesis of BP, that is, complete prevention of explosion is impractical. In addition to the loading capacity of a glass ampule, the explosion is also related to the vacuum-sealing of the glass ampule, which is difficult to control. Hence, an optimal technique to prevent any danger from the explosion during the BP synthesis by the CRT method is to enclose the glass ampule in a flange-fitted stainless-steel tube or any similar closed stainless tube, as shown in Figure 1, and then to employ the heat treatment.

The reaction mechanism for the synthesis of BP from red P using the CTR method is proposed in previous studies. It is expected that red P vaporizes into elemental P or P₄ on heating in a closed glass ampule. The elemental P or P₄ thereafter forms a transitional complex with Sn and I that precipitates as crystals while cooling the glass ampule. Because red P is immediately vaporized into elemental P or P₄ on heating at a high temperature (∼873 K), it is expected that BP should crystallize, notwithstanding immediate cooling of the ampule. Thus, retaining the glass ampule at a high temperature for a

### Table 1. Experimental Parameters of the Dimensions of Glass Ampules, Ratios of Reactants, and Estimated Pressures in Ampules

| x/cm | y/cm | d/cm | V/cm³ | red P/mg | max temp/K | SnI₄/Sn/P (weight) | pressure of P at max temp/MPa | result |
|------|------|------|-------|----------|------------|-------------------|-----------------------------|--------|
| 10   | 0.85 | 0.075| 5.7   | 223      | 873        | 1:1:16            | 9                           | synthesized |
| 12   | 0.85 | 0.075| 6.8   | 197      | 873        | 1:2:18            | 7                           | synthesized |
| 14   | 0.85 | 0.075| 7.9   | 404      | 863        | 1:2:32            | 12                          | exploded   |
| 12   | 0.85 | 0.075| 6.8   | 407      | 873        | 1:2:17            | 14                          | synthesized |
| 13   | 0.60 | 0.100| 3.7   | 222      | 911        | 1:3:18            | 15                          | exploded   |
| 13   | 0.60 | 0.100| 3.7   | 210      | 873        | 1:2:21            | 13                          | synthesized |
| 12   | 0.60 | 0.100| 3.4   | 200      | 873        | 1:2:17            | 14                          | synthesized |
| 7    | 1.00 | 0.120| 6.2   | 275      | 903        | 1:3:17            | 11                          | exploded   |
| 15   | 1.00 | 0.150| 11.7  | 906      | 823        | 1:2:40            | 17                          | exploded   |
| 17   | 1.55 | 0.150| 32.1  | 992      | 823        | 1:2:44            | 7                           | synthesized |
| 12   | 1.00 | 0.150| 9.4   | 802      | 823        | 1:2:40            | 19                          | synthesized |

“A schematic of the ampule is shown below the table.
long period is not necessary, as reported in earlier studies.\textsuperscript{21–24} To account for this, we employed an immediate cooling down procedure after heating the glass ampule to temperatures 873, 823, and 773 K. A typical heating and cooling pattern is shown in Figure 2. In this rapid synthesis procedure, the glass ampule containing the reactants in a fixed ratio is programmed to be heated to temperatures 873, 823, and 773 K over 2 h, followed by immediate commencement of steady cooling (100 K/h) of the furnace temperature. At 450 K, the power switch of the furnace was turned off, and the furnace was allowed to cool to room temperature. The flange-fitted stainless-steel tube containing the glass ampule was thereafter removed from the furnaces.

Optical images of the crystals formed in the three glass ampules heated to various temperatures are shown in Figure 2b. It is evident that BP crystals are formed by employing the immediate cooling down procedure after heating the glass ampule to 823 and 873 K. Therefore, retaining the glass ampule at a high temperature for ~20 h to 10 days as reported in previous studies is not necessary. From several collections of successful events in the synthesis of BP, the minimum synthesis time was estimated to be approximately 5 h. We observed that no BP crystal was formed if the maximum heating temperature is 773 K.

The quality and the reaction yield of BP synthesized by the CTR method, wherein the glass ampule is enclosed in a flange-fitted stainless-steel tube, are similar to those reported by previous studies.\textsuperscript{22–24} To investigate the quality, the synthesized BP was characterized by X-ray diffraction (XRD), Raman analysis, and XPS. Typical XRD and Raman spectra of the as-prepared BP crystals are shown in Figure 3. Three characteristic peaks of BP were observed. The three peaks are assigned and ascribed to $A_k^4$ (out-of-plane, 360 cm\(^{-1}\)), $B_{2g}$ (in-plane to zigzag orientation, 437 cm\(^{-1}\)), and $A_k^2$ (in-plane to armchair orientation, 464 cm\(^{-1}\)).\textsuperscript{25–27} The XRD peaks representing (020), (040), (060), and (080) show a highly preferential orientation along the (0k0) direction without further phases. This indicates high purity and well-crystallized BP.

Figure 3. (a) Raman spectrum of the as-grown BP crystal. Three different peaks and associated modes are indicated. (b) XRD pattern of the as-grown BP. Diffraction peaks from different crystal planes are indicated.

Note that the impurities in the synthesized BP are not traceable in the optical images, Raman spectra, and XRD spectra. Hence, XPS measurements were performed for the elemental analysis of the synthesized BP. Figure 4 shows the wide-range XPS spectra of the as-prepared BP flake. We observe that, in addition to the P 2s and P 2p peaks, the Sn- and I-related peaks are observed at 488.4, 497.2, 620.0, 631.0, 718.0, and 760.0 eV. These peaks are assigned as Sn 3d, I 3d, and Sn 3p, as shown in Figure 4a. Peaks corresponding to O 1s and C 1s are also observed. If the upper layer of the BP flake is removed by exfoliation using scotch tape and the freshly cleaved BP is immediately loaded into the XPS chamber, no Sn- and I-related peaks are observed in the measured XPS spectrum, as shown in Figure 4b. It is known that BP undergoes rapid ambient oxidation. The minor O 1s peaks in the spectrum of the freshly cleaved BP are owing to the ambient oxidation of BP before loading into the vacuum chamber. The minor C 1s peaks are believed to be caused by the intrinsic impurities in the source materials. The high-resolution P 2p peak consists of two components at 130.3 and 131.2 eV (Figure 4c). The single component of P 2s peaks (Figure 4d) and the separation and intensity ratio (3:2) of the two components of the P 2p peak indicate the pure and single state of P atoms in the BP flake.\textsuperscript{28} Thus, the removal of Sn and I impurities simply by exfoliating the upper layer of the BP flake indicates that the impurities are accumulated only on the upper layer of the BP crystal, that is, Sn and I accumulated during cooling to room temperature, whereas the BP earlier crystallized at higher temperatures.

The Sn and I impurities on the upper layer of BP synthesized by the CTR method are inevitable. The exfoliation technique discussed above can be effectively applied to large-size BP flakes or crystals. However, the exfoliation technique cannot be applied on small flakes or needle-shaped crystals. Hence, other purification methods of BP are highly desirable.
Because Sn and I accumulate on the BP surface after complete crystallization of BP at higher temperatures, it is expected that these impurities should be removed by vacuum annealing at some temperature. Hence, the BP flakes were vacuum-annealed at different temperatures. The XPS investigation of the BP flakes after annealing at various temperatures indicated that the I impurities could be effectively removed by vacuum annealing the BP at 600 K. However, the Sn impurities remain in the BP sample. Note that vacuum annealing above 700 K vaporizes all the BP crystals. We found that treating BP with HCl solution can effectively remove the Sn impurities from the BP synthesized by the CTR method. Thus, the Sn and I impurities in BP can be completely removed by a combination of vacuum annealing and HCl treatment.

3. CONCLUSIONS

Frequent explosion of the glass ampule during the high-temperature synthesis of BP by the CTR method is inevitable. In addition, the time required for the synthesis of BP by the CTR method is reported to be approximately 20 h to 10 days. Here, we report a safe and rapid synthesis by the CTR method and a purification procedure for BP. Hazards from the explosions can be prevented by enclosing the glass ampule containing the reactants (red P, Sn, and SnI4) in a flange-fitted stainless-steel tube without compromising the yield and the quality of the BP. In contrast to retaining the glass ampule at a high temperature for approximately 20 h to 10 days, the BP crystal can be successfully synthesized by immediately cooling the glass ampule at 100 K/h after reaching the desired maximum temperature (~873 K) in 2 h. The estimated minimum time for BP synthesis is ~5 h. The as-prepared BP predominately contains Sn and I impurities in the upper layers of the BP flakes. These impurities can be removed by simply exfoliating the upper layers of the flakes or by a combination of vacuum annealing at ~ 600 K and HCl treatment.

4. EXPERIMENTAL SECTION

By varying ratios, red P (Sigma-Aldrich, ≥97.0%), tin (Sigma-Aldrich, 99%, trace metal basis), and tin(IV) iodide (Sigma-Aldrich, 99.999%, trace metals) were loaded in a glass ampule that was vacuum-sealed using an oxygen burner. The glass ampule was thereafter placed in a flange-fitted stainless-steel tube. The glass ampule in the stainless tube was then heated to a specific temperature and retained at the temperature for some period, and subsequently steadily cooled to room temperature. To optimize the crystal formation time and the safest crystal formation conditions, different patterns of heating and cooling procedures were employed on glass ampules with varying dimensions. The prepared BP crystals were characterized by XRD, Raman spectroscopy, XPS, and scanning electron microscopy. The XRD measurements were conducted at room temperature using a RINT 2200VF instrument. The Raman measurements of BP were performed using a Nicolet Almega XR Raman spectrometer with a 532 nm laser. The XPS data were obtained using an AXIS-NOVA XPS system using an Al Kα X-ray source. The incident and emission angles were 60 and 0° to the surface normal, respectively. The analyzer pass energies for the wide range and high-resolution measurements were set to 160 and 20 meV, respectively.

■ AUTHOR INFORMATION

Corresponding Author
Md Zakir Hossain — Gunma University Initiative for Advanced Research (GIAR), Gunma University, Kiryu, Gunma 371-8510, Japan; orcid.org/0000-0002-8193-3018; Email: zakir@gunma-u.ac.jp

Authors
Shunya Kitada — Gunma University Initiative for Advanced Research (GIAR), Gunma University, Kiryu, Gunma 371-8510, Japan
Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c00404

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This work was partly supported by a Grant-in-aid from Japan Society for the Promotion of Science (JSPS). (KAKENHI grant no. 16K04883). The authors are thankful to Prof. Jun-ichi Ozaki of Gunma University for supporting Raman spectral measurements.

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