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Effective treatment of hydrogen boride sheets for long-term stabilization

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Two-dimensional hydrogen boride (HB) sheets prepared via the ion-exchange reaction from magnesium diboride (MgB_2) are known to possess several intriguing properties for a wide range of applications; however, previous reports have shown that the sheets prepared using this method contain small amounts of reactive components, making them unsuitable for certain applications. Therefore, developing a method for preparing HB sheets that exhibit long-term stability and do not contain reactive species is essential. In this study, we developed an effective treatment method for achieving long-term stabilization of HB sheets. We found that by pre-treating the HB sheets with water and then filtering the dried product from an acetonitrile dispersion, we could achieve excellent long-term stability over nine months. This stability was maintained even outside of a glovebox, with no H_2 released by the decomposition and/or reaction. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FT-IR) absorption spectroscopy measurements revealed that the sample exhibited pure HB characteristics with negatively charged boron and B–H–B and terminal B–H bonds, even after nine months of storage. Furthermore, based on thermal desorption spectroscopy (TDS) measurements, the presence of reactive species in the as-prepared HB sheets is attributed to fluctuating B–H bonds with relatively weak binding energies that can be removed using the method developed in this study.

Introduction

Two-dimensional hydrogen boride (HB), or borophane, sheets with a 1:1 H-B molar ratio can be synthesized by the ion exchange of magnesium ions in magnesium diboride (MgB_2) with protons to form a sheet composed of exfoliated boron six-membered rings similar to graphene.¹ Within the six-membered boron rings, the hydrogen atoms are either bridged between two B atoms or bonded on top of a boron atom via three center-two electron (3c-2e) or two center-two electron (2c-2e) bonds, respectively.² These HB sheets are predicted to exhibit intriguing physical and electronic properties,^{3–5} making them suitable for a variety of applications including superior batteries,^{6–8} sensors,⁹ hydrogen storage materials,^{10–12} and current limiters.¹³

Several studies have confirmed that HB sheets exhibit semimetal electronic properties,¹⁴ superior catalytic properties,^{15–19} and specific reductant properties.^{17,20,21} Fujino

et al. demonstrated the ability of HB sheets to catalyze the production of ethylene from ethanol with high selectivity and long-term stability.^{15,16} Similarly, Gao *et al.* found that a catalyst prepared with HB and Pt exhibited superior electrocatalytic activity and stability against oxygen reduction compared to commercial Pt/C for proton exchange membrane fuel cells.^{17,18} In another study, Saad *et al.* reported that a Co_3O_4 catalyst prepared with HB exhibited excellent performance for oxygen evolution.¹⁹ Moreover, studies have shown that CO_2 can adsorb on hydrogen-deficient HB sheets at approximately 300 K, and CO_2 was converted to CH_4 and C_2H_6 above 423 K via dissociation and hydrogenation of CO_2 , as well as C–C coupling, even at relatively low temperatures.²²

HB sheets have redox potentials between -0.277 and -0.257 V versus the standard hydrogen electrode, enabling them to selectively reduce metal ions in solution and form nanoclusters on the sheets.^{20,21} This property makes HB sheets useful as reducing agents. Moreover, ultraviolet (UV) irradiation at 300 K can cause H_2 to be released from the HB sheets as a decomposition product,²³ making them a controllable source of H_2 emission. Furthermore, the formation of HB sheets has paved the way for the conceptual development of new types of HB materials.^{24–32}

To effectively utilize HB sheets for such applications, long-term stability is crucial. Rojas *et al.* reported that HB sheets prepared through ion exchange with MgB_2 are chemically stable but contain a small amount of chemically reactive components when mixed with water. The origin of the chemical stability of HB against water is originated from the negatively charged boron species that are protected by a boron network.³³ In this

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study, we propose an effective treatment method for producing HB sheets with long-term stability.

Experimental

Preparation of HB sheets

HB sheets were synthesized using the previously reported ion-exchange method (the ion-exchange reaction here is $\text{MgB}_2 + 2\text{H}^+ \rightarrow \text{Mg}^{2+} + 2\text{HB}$).¹ The acid-assisted reaction reported in a recent study³⁴ was not employed to avoid the inclusion of used acid species in the product. MgB_2 powder (1.0 g, 99%, Rare Metallic Co. Ltd, Tokyo Japan) was sonicated in an acetonitrile (300 mL, 99.5%, FUJIFILM Wako Chemical Industries Co. Ltd. Osaka Japan) for 40 min with an ASU-10M (AS ONE Cleaner, 40 kHz, 240 W) ultrasonic wave. Thereafter, the acetonitrile with MgB_2 was transferred to a Schlenk flask, and 60 mL of an H-type ion-exchange resin (Amberlite IR120B H, Organo Co. Ltd. Tokyo Japan) was added. Prior to its addition, the resin was acidified by treatment with 0.1 M hydrochloric acid (over 95%, FUJIFILM Wako Chemical Industries Co. Ltd. Osaka Japan) and then washed with distilled water to remove excess acid. The resin was then washed another 10 times with 50 mL of acetonitrile to remove any residual water. The flask was evacuated using a rotary pump equipped with a cold trap and then purged with argon at atmospheric pressure and room temperature (~ 298 K). The mixture was stirred at 360 rpm in an argon atmosphere at room temperature (~ 298 K). After 3 days, it was filtered in argon atmosphere using a 0.2 μm membrane filter. The process was sensitive to water because the hydrolysis of MgB_2 could cause the formation of boric acid as a by-product.³⁵ To remove small amounts of boric acid that inevitably form, the filtrate was placed in a 253 K freezer 20 h, filtered again through a 0.2 μm membrane filter, evacuated using a rotary pump equipped with a cold trap at 323 K for 2 h, and then dried in a 343 K oil-bath for 40 min. The resulting sample was named “as-prepared HB.”

Treatment of HB for long-term stability

As previously reported,³³ the as-prepared HB contains a small amount of reactive components against water and/or oxygen in the air. To remove these reactive components, we treated the as-prepared HB as illustrated in Scheme 1. In step 1, 223 mg of the as-prepared HB was treated with 10 mL of H_2O at 298 K; that is, we intentionally induced the degradation reaction of the reactive part of HB. The gas generated by the reaction was collected through the water displacement method to evaluate

the extent of the reaction in the as-prepared HB. After the reaction, the water with HB was dried for a week under argon flow (30 mL min^{-1}) in a 343 K water bath (step 2). The dried sample was then redissolved in 30 mL of acetonitrile (step 3) and filtered through a 0.2 μm membrane filter (step 4). Steps 2–4 were conducted for the separation of non-reactive HB from the boric acid, which is the reaction product of water with reactive HB. Thereafter, the filtrate was dried under argon flow (50 mL/min) in a 343 K water bath for a week (step 5) to obtain a “purified HB” sample. The purified HB was divided into four aliquots (we have prepared two sets of four aliquots), which were analyzed by X-ray photoelectron spectroscopy (XPS) after 1, 3, 6, and 9 months of storage under the following conditions: (1) refrigerated storage (in a cold (279 K) and dark environment); and (2) ambient storage (room temperature: 288–301 K) on a desk facing a window (about 7000 Lux for a few hours on sunny days and less than 1000 Lux otherwise) to evaluate their long-term stability. We also analyzed the as-prepared HB stored in a glovebox over 9 months. To examine the effects of the treatment, another sample (named “as-treated HB”) was also prepared without steps 3–5.

Characterization

XPS measurements were performed using a JEOL JPS-9010 TR spectrometer equipped with an ultrahigh vacuum chamber and an Mg $\text{K}\alpha$ X-ray source (1253.6 eV). The pass energy was 10 eV, the energy resolution (estimated from the Ag $3d_{5/2}$ peak width of a clean Ag sample) was 0.635 eV, and the binding energy uncertainty was ± 0.05 eV. The sample was mounted on graphite tape, and the Shirley background was subtracted from the spectrum using SpecSurf version 1.8.3.7 (JEOL, Ltd., Japan). The charge build-up in the sample due to incomplete contact between the graphite tape and sample holder resulted in a slight shift to higher binding energies in the spectra. Therefore, we used the C 1s peak of the graphite tape at 284.6 eV as a reference to calibrate the charge build-up. The oxidation states of boron were determined by comparing the B 1s core level peak position with literature values (listed in the Supplementary Information of Ref. ³⁶).

Fourier transform infrared (FT-IR) absorption spectroscopy measurements were performed at ~ 300 K using benchtop IR equipment (ALPHAII, Bruker, Billerica, MA, USA). For comparison, we also conducted FT-IR measurements of commercial boric acid (FUJIFILM Wako chemical Industries Co. Ltd.).



Scheme 1 Treatment of HB sheets for long-term stability.

Thermal desorption spectroscopy (TDS) of H₂ was performed using a thermogravimetric analyzer (STA-2500 Regulus, NETZSCH, Tokyo Japan). The exhaust gas was simultaneously analyzed by a quadrupole mass spectrometer (MKS, Microvision 2) in a home-build ultra-high vacuum chamber by sampling gas through a capillary connection.

The weight densities of as-prepared HB and purified HB were evaluated by dividing the measured weight by apparent volume of the cylinder pellet (diameter of 10 mm), which was prepared by applying pressure of 35 MPa to powders in pellet-molding-machine using hydraulic press (High Pressure Jack J-1, AS ONE Corp.). Approximately 100 mg powder was used and resulting pellet was found to have width of approximately 1.0 mm. The exact weight was measured by analytical balance (Cubis II MCA524S-2S01-U, Sartorius Japan Ltd., Tokyo) within 0.1 mg accuracy, and width of the pellet was measured by ruler within 0.1 mm accuracy.

The gas collected during step 1 of treatment was analyzed by a thermal conductivity detector (TCD) gas chromatograph (GC-8A, Shimadzu Co. Ltd. Kyoto Japan) equipped with a molecular sieve 5A column. To analyze the gas species released from each aliquot stored in a closed cell (after step 5), 0.5 mL of

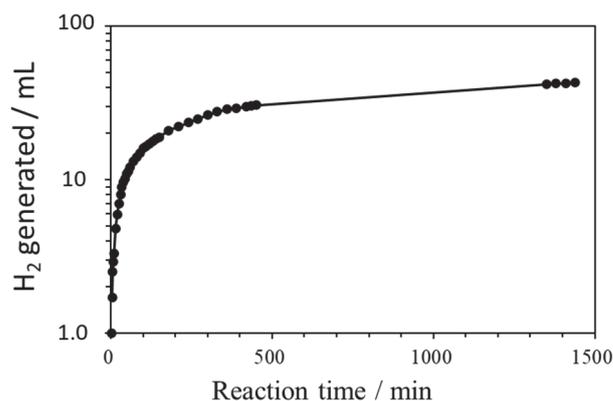


Fig. 2 Hydrogen generation from the reaction of as-prepared HB with water at 298 K.

the sampling gas was extracted using a syringe from the hole at the top of the cell (the hole was prepared beforehand and closed during storage) and analyzed by the same TCD gas chromatograph after 1, 3, 6, and 9 months. The generated total amount of gas in cell (21.8 mL) was then calculated from the amount of the sampling gas by assuming that the gas was equally distributed in the cell.

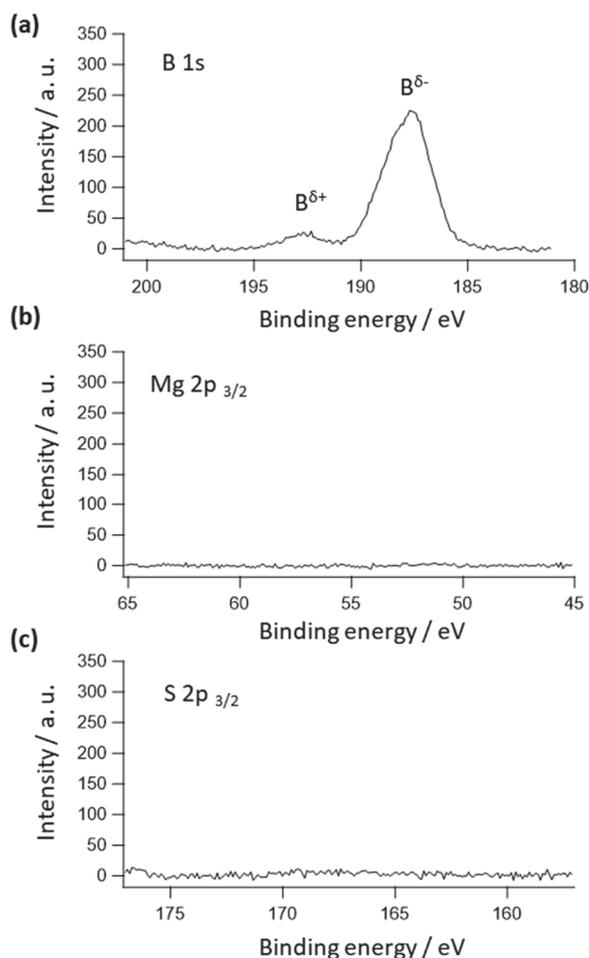


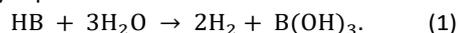
Fig. 1 XPS results of the HB sheets prepared by the traditional method (as-prepared HB). Core level spectra of (a) B 1s, (b) Mg 2p_{3/2}, and (c) S 2p_{3/2}.

Results and discussion

Treatment of HB for long-term stability

Fig. 1 shows the XPS results for B 1s, Mg 2p_{3/2}, and S 2p_{3/2} in the as-prepared HB. The B 1s spectrum shows two peaks at 187 and 193 eV, with no peak detected in the Mg 2p_{3/2} and S 2p_{3/2} regions. These results suggest that the MgB₂ reacts through the ion-exchange reaction ($\text{MgB}_2 + 2\text{H}^+ \rightarrow 2\text{HB} + \text{Mg}^{2+}$) and the as-prepared HB does not contain any unreacted MgB₂ or ion-exchange resin (which contains sulfur). The B 1s peak at 187 eV can be attributed to the negatively charged boron (B^{δ-}) present in HB,^{1,2,33} whereas the peak at 193 eV corresponds to the positively charged (oxidized) boron (B^{δ+}), which could be due to the reaction of HB with water and/or oxygen after its preparation,^{1,2,33} based on the chemical shift of core level electron energy (in the case of boron, the negatively charged boron such as the one in metal boride shows the B 1s peak at 186.3–188 eV, while the oxidized boron such as the one in B₂O₃ shows the B 1s peak at 192–195 eV, as listed in the Supplementary Information of Ref.³⁶).

Upon adding water to the as-prepared HB sheets, the reaction is initiated, resulting in the evolution of H₂ gas, as confirmed by gas chromatography; no other gases were detected. The H₂ release rate gradually decreases and almost ceases after 24 h (Fig. 2). These results suggest that the following reaction occurs partly in the as-prepared HB, as previously reported:³³



A total of 42 mL H₂ was generated, which is equivalent to 1.88×10^{-3} mol in the standard state. Based on eqn (1), half of the generated H₂ is assumed to originate from the HB sheets, which amounts to approximately 5% of the hydrogen content in the HB

sheets. As previously reported, the powder obtained by drying the mixture of HB and water contains unreacted HB and traces of boric acid, and no longer reacts with water.³³

The weight densities of as-prepared HB and purified HB were found to be almost the same as 1.26 ± 0.10 g/cm³. The FT-IR spectrum of the as-prepared HB (Fig. 3(a)) exhibits two

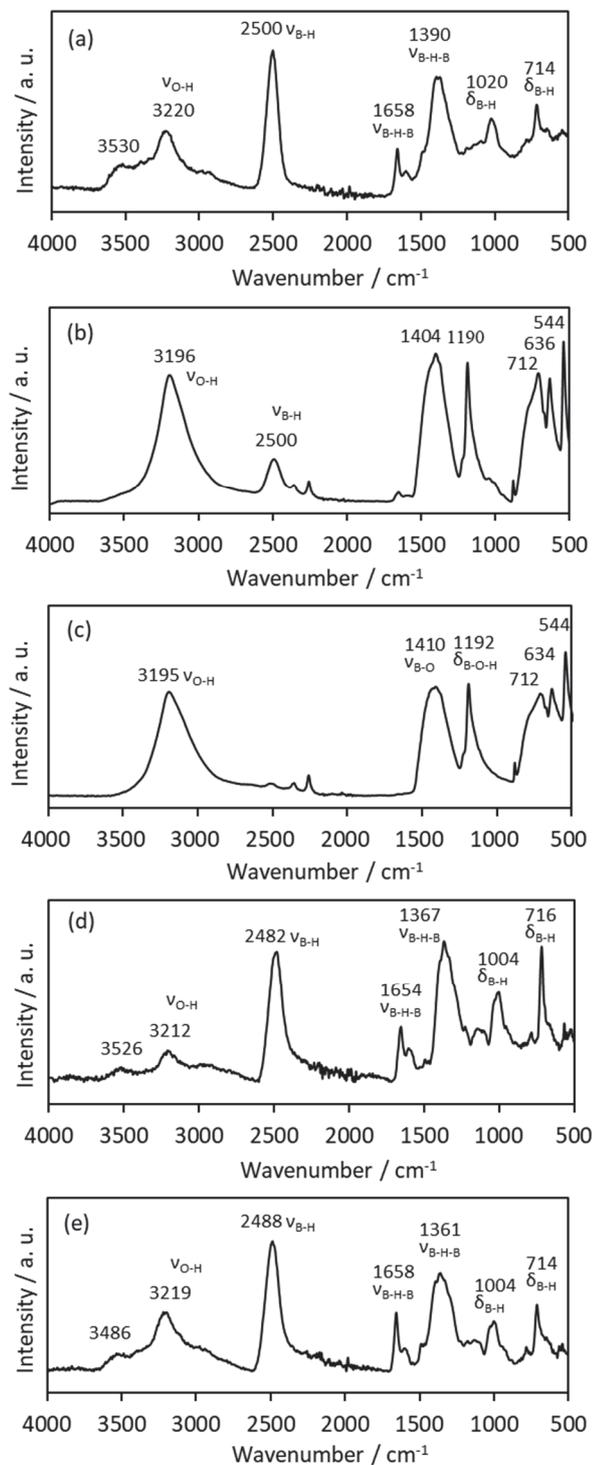


Fig. 3 FT-IR spectra of the (a) as-prepared HB, (b) as-treated HB, (c) commercial boric acid, (d) purified HB, and (e) purified HB after 9 months of refrigerated storage.

absorption bands at 714 and 1020 cm⁻¹, which are assigned to B–H bending, and at 1390 and 1658 cm⁻¹, which are assigned to bridge-bonded B–H–B stretching.^{2,33} Additionally, a prominent and intense absorption band at 2500 cm⁻¹ is assigned to terminal B–H stretching.^{1,2,33} A small amount of water was adsorbed on the HB sheets as indicated by the peaks at approximately 3220 and 3530 cm⁻¹. The FT-IR spectrum of the as-treated HB (Fig. 3(b)) is similar to that of the commercial boric acid (Fig. 3(c)), except for the B–H stretching peak at 2500 cm⁻¹. Vibrational modes observed in both spectra include O–B–O bending (544 cm⁻¹), BO₃ bending (634 cm⁻¹), O–H torsion (712 cm⁻¹), B–O–H bending (1192 cm⁻¹), B–O stretching (1410 cm⁻¹), and O–H stretching (3195 cm⁻¹),^{37–39} indicating that the surface of the as-treated HB is mainly composed of boric acid. The spectrum of the purified HB (Fig. 3(d)) closely resembles that of the as-prepared HB, suggesting successful removal of boric acid in steps 3–5. The spectrum of the purified HB after 9 months of refrigerated storage (Fig. 3(e)) exhibits absorption bands corresponding to B–H and B–H–B stretching vibrations, along with a minor amount of adsorbed water. These bands closely resemble those observed in Figs. 3(a and d), indicating that the purified HB maintains its characteristic features, even after 9 months of storage outside of a glovebox. The FT-IR spectrum shown in Fig. 3(a) can also be obtained by storing the as-prepared HB in a glovebox over 9 months.

The XPS B 1s core-level spectrum of the as-treated HB (Fig. 4(a)) shows a larger peak intensity at 194 eV (B^{δ+}) than at 187 eV (B^{δ-}), indicating that boron in the HB sheets partially reacted with water, resulting in the formation of a minor amount of boric acid mainly on the surface of the product. Despite this dominant B^{δ+} peak, the actual amount of oxidized boron separated by filtration (steps 3–5 in Scheme 1) is considerably smaller than expected. The purified HB (with 100% B^{δ-}) weighs 171 mg, which accounts for 77% of the initial weight of the as-prepared HB (223 mg). Therefore, the dominant oxidized peak in Fig. 4(a) is attributed to the presence of the reacted species on the surface of the product rather than throughout the sample. The amount of HB remaining after purification (purified HB) is consistent with the amount of unreacted HB (95%) estimated from the results shown in Fig. 2. The apparent decrease in the amount of purified HB from 95% to 77% is due to additional sample loss during treatment: specifically, the HB samples adsorbed on boric acid are separated together with boric acid in the process of separation. The purified HB exhibits a consistent single peak at 187 eV (B^{δ-}) after 1, 3, 6, and 9 months (Figs. 4(b, c, d, and e), respectively). These results suggest that the purified HB does not form boron oxides, even after 9 months of storage outside of the glovebox, which is consistent with the FT-IR results (Fig. 3). Furthermore, the similarities in the XPS B^{δ-} peaks for the purified HB stored on a desk facing a window (Figs. 4(f–i)), suggests that it remains stable for a period 9 months.

Kawamura *et al.* reported that intense UV light can cause H₂ emission from HB sheets.²³ Therefore, it was a matter of concern that storing HB on a desk facing a window for an extended period might cause a trace amount of H₂ to be released owing to the presence of UV radiation in sunlight (~6%).

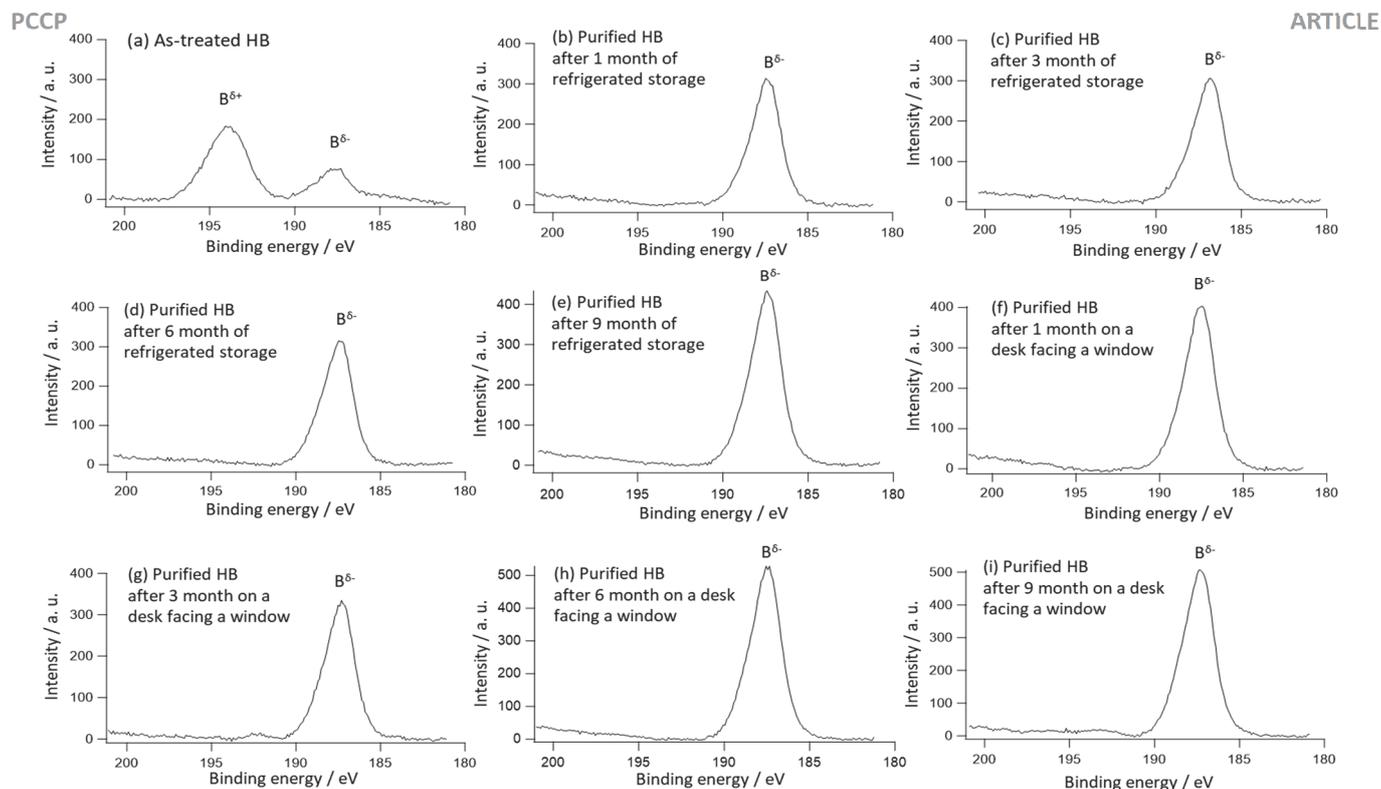


Fig. 4 XPS B 1s core-level spectra of the (a) as-treated HB; purified HB after (b) 1 month, (c) 3 months, (d) 6 months, and (e) 9 months of refrigerated (dark and cool) storage; purified HB after (f) 1 month, (g) 3 months, (h) 6 months, and (i) 9 months kept on a desk facing a window.

However, the absence of changes in the XPS $B^{\delta-}$ peak (Fig. 4) suggests that there was no damage due to sunlight irradiation, even after 9 months.

To assess the potential damage to the HB below the detection limit of XPS, we directly analyzed the gas species released from the purified HB stored in a closed cell for 1, 3, 6, and 9 months via gas chromatography (Fig. 5). Only a trace amount of H_2 and no other gases were formed during storage. The H_2 released from the purified HB when stored on a desk facing a window (Fig. 5(b)) is potentially UV light-induced; 4.95×10^{-4} mol H_2 is released per gram of HB after 9 months, corresponding to the 1.2% of hydrogen in HB. It is noteworthy that Kawamura et al. reported that low-intensity UV irradiation did not cause the significant release of H_2 from HB,²³ which is consistent with our findings; that is, only 1.2% of hydrogen was released even after 9 months of storage on a desk facing a window. The origin of this trace amount of hydrogen release may be related to the specific defect sites of HB, which are more sensitive to UV irradiation, even at weak intensities. A more careful analysis is required to fully understand this phenomenon.

Origin of the long-term stability

The TDS profile for the as-prepared HB (Fig. 6(a)) exhibits large desorption peaks at 466 and 515 K, followed by continuous desorption for a broad temperature range, which is consistent with previous reports.^{1,2} However, the peaks observed at lower temperatures (400 and 430 K) were not reported in the literature.^{1,2} The presence of these peaks may be attributed to

the lower temperature (343 K) used during the synthesis of HB in our study compared to previous studies (363 K^{1,2}). The multiple desorption peaks in Fig. 6(a), including the 466 K peak, suggest the presence of various types of H–B bonding configurations (e.g., variations in the sizes of HB sheets and/or the densities of defects in the HB). Furthermore, the intensity of the desorption peak around 400 K varies among the samples,

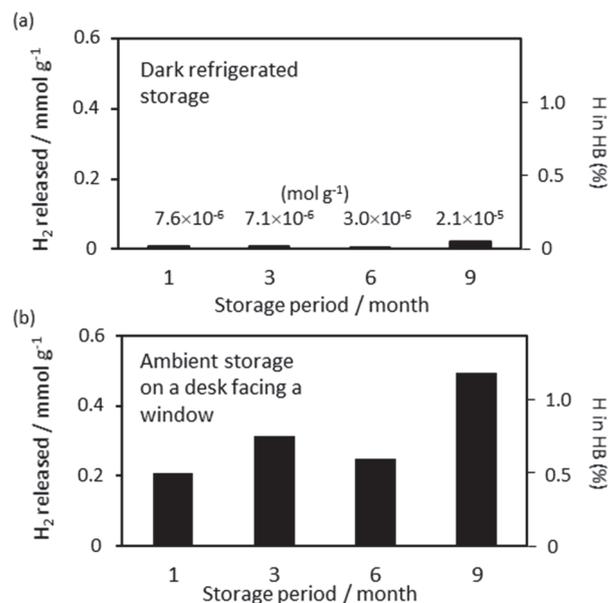


Fig. 5 H_2 release from purified HB during long-term storage (a) in a dark refrigerator and (b) on a desk.

and the lower-temperature peaks seem to merge into a single

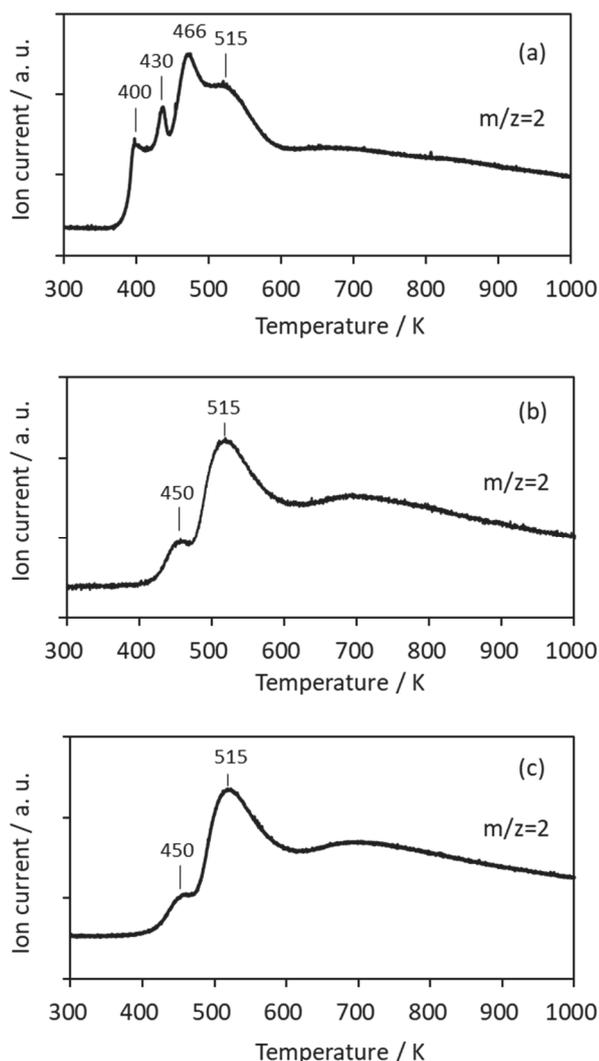


Fig. 6 TDS profiles for the as-prepared HB (a) and the purified HB after (b) 1 month and (c) 9 months of refrigerated storage. m/z: mass-to-charge ratio.

broader, less distinct peak for the purified HB (Figs. 6(b and c)), indicating the effectiveness of the treatment method (steps 1–5 in Scheme 1) in removing the reactive species from the HB. We therefore hypothesize that the species in HB that react with water (eqn (1)) correspond to the lower-temperature desorption peaks. Theoretical calculations have shown that the boron in HB maintains a negative charge owing to strong boron bonding networks, which effectively shield it from reacting with the negatively charged oxygen in water.³³ This is a key factor contributing to the chemical stability of HB in water. The reactivity of boron in HB derives from its ability to temporarily carry a positive charge, as seen in the case of diborane (B_2H_6). When B_2H_6 reacts with water, it is temporarily converted to BH_3 , during which, the boron atoms become oxidized,³³ rendering them more reactive toward negatively charged oxygen in water. Such fluctuating B–H bonds may exist in the as-prepared HB with relatively weak binding energies; however, these bonds can be broken through the treatment method developed in this study (steps 1–6 in Scheme 1).

Conclusions

In this study, we developed an effective method for treating HB to ensure long-term stability (up to nine months) by removing unstable species inevitably included in the synthesized product by ion-exchange of MgB_2 . The results were verified by XPS and FT-IR absorption spectroscopy. HB sheets subjected to water-mixing and filtration with an acetonitrile solution before drying showed pure HB characteristics, with negatively charged boron and B–H–B and terminal B–H bonds even after nine months of storage outside of a glovebox. The TDS results revealed that the reactive species in the as-prepared HB are attributed to the presence of fluctuating B–H bonds with relatively weak binding energies. The developed method can be used to effectively utilize HB sheets for predicted and/or reported intriguing applications.

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