Formation Mechanism of Boron-Based Nanosheet through the Reaction of MgB₂ with Water

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ABSTRACT: A recent experiment demonstrated that ultrasonication of MgB₂ in water yields Mg-deficient hydroxyl-functionalized boron nanosheets at room temperature. Herein, we examined the mechanism of nanosheet formation. Analysis of the reaction products and temporal variation in pH and H₂ production shows that the reaction between MgB₂ and water comprises two steps: (i) an ion-exchange process between protons and a part of Mg cations of MgB₂ with its exfoliation and (ii) the hydrolysis reaction between Mg-deficient boron hydride and water to produce H₂ and Mg-deficient hydroxyl-functionalized boron sheets. The sheets with a stacking periodicity of 0.70 nm were obtained as the supernatant of the reaction product of water with MgB₂. The stacking sheets can be further exfoliated if the reaction is conducted under ultrasonication. The derived nanosheets are composed of sp²-bonded boron framework and possess a disordered structure containing hydroxyl species and oxidized magnesium.

1. INTRODUCTION

A two-dimensional (2D) boron sheet (borophene) was recently synthesized by the deposition of boron atoms on a Ag(111) surface following a bottom-up synthesis method.1,2 However, a top-down method for the mass production of borophene, such as a liquid exfoliation method,3 has not been established. With consideration of the application of borophene or borophene-related 2D sheets in a wide variety of fields, such as electronic devices, batteries, catalysts, and hydrogen storage materials as predicted by the theoretical calculations,4,5 it is essential to develop both top-down and bottom-up methods for its production.

We have focused on magnesium diboride (MgB₂), a binary compound composed of hexagonal boron sheets alternating with Mg cations, as the parent material in the top-down approach for borophene or borophene-related 2D sheets. Since MgB₂ inherently contains 2D boron sheets in the material, it is of interest to determine whether borophene could be formed simply by exfoliation and deintercalation of Mg in a top-down approach. According to the recent report, however, ultrasonication of water with MgB₂ at room temperature produces not pure boron sheets but Mg-deficient hydroxyl-functionalized boron nanosheets.6 The presence of Mg and hydroxyl species in nanosheets is probably caused by the instability of charged boron sheets in water derived from MgB₂ by the exfoliation. We thus consider that the designed ion-exchange method between Mg cations and other cations is the way to produce a borophene-related stable new type of 2D materials in a top-down approach.

From this point of view, the Mg-deficient hydroxyl-functionalized boron nanosheets can be classified as one of the stabilized borophene-related 2D sheets as a reaction

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product of MgB$_2$ and water. It can be obtained simply by the mixture of MgB$_2$ with water at room temperature under ultrasonication and shows an intriguing optical property. However, the reaction mechanism driving the formation of the nanosheets including the role of the ultrasonication is yet to be analyzed. Also, the presence of hydroxyl species in the sheets cannot be simply explained by the ion-exchange process. For the further application of the ion-exchange and liquid exfoliation methods to a metal diboride as the production method of several types of borophene-related 2D sheets, a deeper understanding of the formation mechanism of nanosheets on reaction with water is fundamental and essential. Therefore, we examined the mechanism of formation of nanosheets during a reaction between water and MgB$_2$.

2. METHODS

MgB$_2$ powder (99%, 100 mesh size, rare metallic) was mixed with distilled water at room temperature under ultrasonication and shows an intriguing optical property. However, the reaction mechanism driving the formation of the nanosheets including the role of the ultrasonication is yet to be analyzed. Also, the presence of hydroxyl species in the sheets cannot be simply explained by the ion-exchange process. For the further application of the ion-exchange and liquid exfoliation methods to a metal diboride as the production method of several types of borophene-related 2D sheets, a deeper understanding of the formation mechanism of nanosheets on reaction with water is fundamental and essential. Therefore, we examined the mechanism of formation of nanosheets during a reaction between water and MgB$_2$.

**Figure 1.** (a) Photographs of distilled water after the mixing of MgB$_2$ at room temperature. Photographs of the dried supernatant and precipitate are also shown. (b) Variations in the amount of the H$_2$ produced from water after the mixing of MgB$_2$ with (red ●) or without (blue ▲) ultrasonication. In the case of ultrasonication, ethylenediaminetetraacetic acid chelator was added to the solution at about 8400 min. The plots were generated on the basis of 255 mg of MgB$_2$ and 255 mL of water (in the case of the plot with ultrasonication, 510 mg of MgB$_2$ and 510 mL of water were used, and thus the produced H$_2$ amount was divided by 2). (c) Tyndall effect in a solution containing different amounts (0, 1.6, 5.7, and 11 mg from the left) of the dried supernatant in 5.0 mL of water, when a green laser was introduced from the left. Due to the scattering at the ampule wall, only the region shown by arrows can be used to evaluate the presence of Tyndall effect. (d) Variation of pH of water with time after the mixing of MgB$_2$ without ultrasonication (green △). For the comparison, the results in panel b (H$_2$ amount) are also plotted together.
The FTIR spectrum was measured at room temperature using a FT/IR-300 spectrophotometer (JASCO Analytical Instruments). The sample was analyzed as a KBr pellet. The background signal was subtracted using Spectra Manager Software (JASCO Analytical Instruments).

XPS measurements were performed at room temperature using a JPS 9010 TR (JEOL, Ltd., Japan) with an ultrahigh vacuum chamber and an Al Kα X-ray source (1486.6 eV). The pass energy was 10 eV; the energy resolution (estimated from the Ag 3d5/2 peak width of a clean Ag sample) was 0.635 eV, and the uncertainty in the binding energy was ±0.05 eV. The sample was mounted on the sample holder using a graphite tape with a metal contact and introduced into the ultrahigh vacuum chamber for measurement. The Shirley background was subtracted from the spectrum using SpecSurf software (version 1.8.3.7, JEOL, Ltd., Japan). Charge-up in the sample was calibrated the charge-up amount assuming the B 1s binding energy was 188.2 eV.\(^7\)

### 3. RESULTS AND DISCUSSION

#### Reaction Process

Mixing MgB\(_2\) with distilled water at room temperature results in gas production and a black turbid suspension of water (Figure 1a). The produced gas was identified as H\(_2\), which was independently analyzed during the reaction by gas chromatography. As shown in Figure 1b, H\(_2\) production saturated at about 6000 min with a total H\(_2\) production of about 150 mL, when 255 mg of MgB\(_2\) in 255 mL of water was used in a reaction without ultrasonication. The saturation amount of H\(_2\) (6.25 mmol) corresponds to about 1.1 times excess compared with Mg atoms in the starting material (5.55 mmol). These results indicate that H\(_2\) was produced as the major reaction product between MgB\(_2\) and water.

After saturation is attained with respect to H\(_2\) production, the water in the reaction medium containing MgB\(_2\) becomes relatively transparent with the formation of a precipitate (Figure 1a), suggesting that the reaction reaches an equilibrium and the reaction products are separated as hydrogen gas, precipitate, and a colloid suspended in the solution. As evidence indicating the presence of colloidal in the solution, a distinct Tyndall effect, confirming the formation of the colloid, was observed in the aqueous solution with dried supernatant, as highlighted by the arrows in Figure 1c. The incident green laser was scattered in the solution, and its intensity increases with an increase in the density of the dried supernatant in water.

The time required for the saturation of H\(_2\) production becomes much shorter when the reaction was carried out under ultrasonication, as shown in Figure 1b. The total amount of H\(_2\) produced is not significantly different (though slightly larger) compared with the reaction without ultrasonication. The total weights of precipitate and dried supernatant are comparable between the reaction conditions (with and without ultrasonication) as shown in Table 1. It can be concluded that ultrasonication promotes the reaction probably by increasing the frequency factor for the reaction, while the fundamental chemical reaction between MgB\(_2\) and water is essentially the same with and without ultrasonication.

Figure 1d shows the temporal variation in the pH of water after the mixing of MgB\(_2\) without ultrasonication. A significant increase in pH from 6.0 to 10.5 was observed within about 1.5 min. This is in sharp contrast to temporal variation in H\(_2\) production; that is, the production of H\(_2\) is almost zero at 1.5 min even with ultrasonication as shown in Figure 1d. This difference indicates that the chemical reaction between MgB\(_2\) and water, including H\(_2\) production, is not a single process but comprises multiple steps. The pH variation can be explained by the chemical reaction Mg(OH)\(_2\) → Mg\(^{2+}\) + 2OH\(^-\) in water, taking into account the solubility of Mg(OH)\(_2\) (9 mg/L).\(^9\) That is, the pH of water containing a saturation amount of soluble Mg(OH)\(_2\) is estimated to be 10.49, which is almost identical to the pH at the saturation condition in Figure 1d (pH = 10.5).

<table>
<thead>
<tr>
<th>sample</th>
<th>dried supernatant (g)</th>
<th>precipitate (g)</th>
<th>total (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-MgB(_2):1 g H(_2)O:500 mL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>lot 1</td>
<td>1.66</td>
<td>0.94</td>
<td>2.60</td>
</tr>
<tr>
<td>lot 2</td>
<td>1.72</td>
<td>1.17</td>
<td>2.89</td>
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<tr>
<td>with ultrasonication</td>
<td>1.65</td>
<td>1.30</td>
<td>2.95</td>
</tr>
<tr>
<td>c-MgB(_2):1 g H(_2)O:500 mL</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>lot 1</td>
<td>1.50</td>
<td>0.94</td>
<td>2.44</td>
</tr>
<tr>
<td>lot 2</td>
<td>1.53</td>
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<td>2.54</td>
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<tr>
<td>with ultrasonication</td>
<td>1.55</td>
<td>0.85</td>
<td>2.40</td>
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<tr>
<td>a-MgB(_2):1 g H(_2)O:500 mL</td>
<td></td>
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<tr>
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<td>3.00</td>
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<tr>
<td>with ultrasonication</td>
<td>1.65</td>
<td>0.78</td>
<td>2.43</td>
</tr>
</tbody>
</table>

Table 1. Weights of Dried Supernatant, Precipitate, and the Summation (Total)\(^a\)

\(^a\)For different experimental lots with different conditions (starting material and with or without ultrasonication) for the reaction between MgB\(_2\) (1 g) and water (500 mL) at room temperature. The calculated weight for the total amount of the assumed reaction Mg(OH)\(_2\) + 2B(OH)\(^-\) is also shown.

The FTIR spectrum was measured at room temperature using a JPS 9010 TR (JEOL, Ltd., Japan) with an ultrahigh vacuum chamber and an Al Kα X-ray source (1486.6 eV). The pass energy was 10 eV; the energy resolution (estimated from the Ag 3d5/2 peak width of a clean Ag sample) was 0.635 eV, and the uncertainty in the binding energy was ±0.05 eV. The sample was mounted on the sample holder using a graphite tape with a metal contact and introduced into the ultrahigh vacuum chamber for measurement. The Shirley background was subtracted from the spectrum using SpecSurf software (version 1.8.3.7, JEOL, Ltd., Japan). Charge-up in the sample was calibrated the charge-up amount assuming the B 1s binding energy was 188.2 eV.\(^7\)

Hydroxyl-functionalized boron is then expected to become a colloid in aqueous solution exhibiting a Tyndall effect (Figure 1c). The weights of dried supernatant and precipitate obtained from 1.0 g of MgB\(_2\) and 500 mL of distilled water at different conditions are shown in
Figure 2. (a) SEM image, (b) TEM images and electron diffraction, (c) EELS spectrum, (d) EDS spectrum, and (e) element mapping (B: peak at 189–214 eV in EELS, Mg, peak at 1.25 keV in EDS, O: peak at 534–560 eV in EELS) of dried supernatant of MgB$_2$ + H$_2$O.

Figure 3. (a) XRD patterns for MgB$_2$, dried supernatant of MgB$_2$ + H$_2$O (without and with ultrasonication). (b) FTIR spectrum of dried supernatant of MgB$_2$ + H$_2$O without ultrasonication.
Table 1. We used three different types of MgB₂ (m-MgB₂, commercial MgB₂; c-MgB₂, synthesized using crystalline boron; a-MgB₂, synthesized using amorphous boron, details in Supporting Information and Figure S1) with or without ultrasonication. In every case, the total weights are slightly larger, but close to the calculated weight of 2.48 g assuming the reaction products are Mg(OH)₂ + 2B(OH). The major reactions for MgB₂ and H₂O can thus be concluded as reactions i and ii. This conclusion is consistent with the results from the SEM, TEM, FTIR, and XRD analyses of precipitate and dried supernatant, which will be described later. The slight difference in weight is probably caused by the different process including the reaction between MgB₂ and H₂O. Indeed, the amount of detected H₂ produced by the reaction (Figure 1b) is about 56−60% that of the expected H₂ amount by the reactions i and ii.

Formation of Nanosheets. Sheets with 100 μm size were observed in SEM and TEM images of the dried supernatant (Figures 2a,b). Observed sheets contain clear bent sections, indicating the flexible nature of the sheets. The sheet thickness can be roughly estimated to be less than 10 nm on the basis of the cross-section of the sheet indicated by arrows in Figure 2b. According to the electron diffraction measurement, no ordered structure was observed (Figure 2b). Conversely, two distinct boron peaks were detected in EELS spectrum as shown in Figure 2c together with a small oxygen peak. Two boron peaks at 188.4 and 195.3 eV can be assigned as EELS peaks originating from the K-shell excitation from B 1s to π* and B 1s to σ*. The sheets are thus suggested to be composed of a sp²-bonded boron framework with a disordered structure. The sp²-bonded boron framework is consistent with the hexagonal structure of boron in the starting material, MgB₂. EDS shows the presence of magnesium and oxygen (Figure 2d). The presence of Mg and O is probably the cause for the disordered structure of the sheet by bonding with boron randomly (possibly by forming sp³-like bonding). Indeed, the observed species (B, Mg, and O) are found to be uniformly distributed in the sheet by STEM, as seen from the elemental mapping shown in Figure 2e. The elemental mapping is constructed by plotting the EELS intensities for B and O (B, peak area at 189–214 eV; O, peak area at 534–560 eV) and EDS intensity for Mg (peak intensity at 1.25 keV).

Clear diffraction peaks were observed in the XRD pattern of the dried supernatant without ultrasonication as shown in Figure 3a, which is in contrast to the electron diffraction measurement (Figure 2b). The observed distinct XRD peak at 12.6° (0.702 nm) and broad, weak peaks at 36.7° (0.245 nm), 59.3° (0.156 nm), 60.8° (0.152 nm), and 61.2° (0.151 nm) are different from peaks observed in case of MgB₂. These peaks were reproducibly observed even for samples derived from different types of MgB₂ (Figure S2). Among them, the distinct peak at 12.6° probably originates from the stacking periodicity of the sheets, since such an intense single peak is known to appear in two-dimensional layered materials such as graphite-intercalated compounds. However, the origin of other peaks is not clear, and it is possible that they could arise either from the sheet or from nanoparticles on the sheet. The possible nanoparticles on the sheet are Mg(OH)₂ particles because the peaks at 36.7° and 59.3° are not different from the (101) and (210) peaks of Mg(OH)₂ (see standard spectrum of Mg(OH)₂ shown in Figure S3), and we occasionally observed nanoparticles on the sheet in TEM images (Figure S4).

Conversely, no XRD diffraction peaks were observed for the dried supernatant when the reaction was carried out under ultrasonication as shown in Figure 3a, suggesting that ultrasonication induces perfect exfoliation of the stacking sheets, so that the flexible monolayer structure causes the absence of the diffraction peaks, as in the case of XRD for the flexible single layer graphene. Significant exfoliation of the sheet due to ultrasonication is consistent with a previous report on Mg-deficient hydroxyl-functionalized boron nanosheets manufactured using ultrasonication, where formation of a.
two-dimensional nanosheet with a thickness of a few layers was reported.\textsuperscript{6} In our current work, we observed an intermediate state between MgB\textsubscript{2} and such hydroxyl-functionalized boron nanosheets as layered sheets with a stacking periodicity of 0.70 nm, as shown in Figure 3a.

The intermediate layered sheets identified in this work contain hydroxyl species as observed by FTIR (Figure 3b), which is consistent with the proposed reaction ii. In the FTIR spectrum, clear BH stretching vibrational modes were also observed as absorptions at 2488 and 1640 cm\textsuperscript{-1},\textsuperscript{14} which is probably due to the unreacted BH in the proposed reaction ii. The latter IR peak corresponds to a BH stretching vibrational mode originating from the three-center two-electron bonds of boron hydrides. We note here that while there are no indications of the formation of B(OH)\textsubscript{3} under the current experimental conditions, B(OH)\textsubscript{3} formation was clearly identified in XRD patterns and FTIR spectra when there is a complete exchange of Mg ions with protons in water using acid.\textsuperscript{15} This is because of the repetitive hydrolysis of borane as in the case of diborane.\textsuperscript{10} In other words, the presence of uniformly distributed Mg in the sheet suppresses the hydrolysis of boron hydrides to form B(OH)\textsubscript{3} but leads to the formation of the Mg-deficient, hydroxyl-functionalized boron nanosheets.

Sample color and XRD patterns of the precipitate significantly depend on the differences in the starting material of MgB\textsubscript{2} (m-MgB\textsubscript{2}, c-MgB\textsubscript{2}, and a-MgB\textsubscript{2}) in contrast to the dried supernatant (Figures S2 and S3). In every case, however, the precipitate contained Mg(OH)\textsubscript{2} as observed in the XRD patterns (Figure S3). This is consistent with our proposed reaction i. The origin of the difference in sample color and XRD patterns is due to the difference of the amount of impurities present in the starting material, such as amorphous boron and hexagonal boron nitride, as they precipitate rather than form colloids in the solution. In other words, impurities in the starting material do not affect the purity of the dried supernatant. Indeed, sample color and XRD of the dried supernatant have no dependence on the starting material (Figure S2).

XPS spectra for the dried supernatant prepared without ultrasonication and those for the starting material MgB\textsubscript{2} are shown in Figure 4. In both cases, boron, oxygen, and magnesium signals are detected. This is consistent with EELS and EDS results (Figure 2c,d). Here, we focus on B and Mg signals in XPS, since oxygen signals originate not only from the sample but also from the graphite tape supporting the sample. In the case of the starting material (MgB\textsubscript{2}), the peak at the lower binding energy (188.2 eV) corresponds to the negatively charged boron species in MgB\textsubscript{2}, while the peak at the higher binding energy (193.2 eV) corresponds to the positively charged boron found in boron oxides such as B\textsubscript{2}O\textsubscript{3} on the MgB\textsubscript{2} surface as reported previously.\textsuperscript{8} The Mg 2p peak from MgB\textsubscript{2} at 51.3 eV is in accordance with the value reported in the literature, which is known to reflect that Mg has a positive charge greater than 0 but less than +2.\textsuperscript{16,17} For the dried supernatant, the B 1s intensity becomes larger and the Mg 2p intensity becomes smaller compared to those of MgB\textsubscript{2}. Quantitatively, the atomic ratio of Mg and B can be estimated as 68.3 and 31.7 atom % (Mg:B = 68.3:31.7) for MgB\textsubscript{2} and 41.1 and 58.9 atom % (Mg:B = 41.1:58.9) for the dried supernatant, on the basis of the peak area with consideration of the sensitivity factors (B 1s, 2.1017; Mg 2p, 1.4025). The significant deviation of the B/Mg ratio from the actual stoichiometric ratio of 2 for MgB\textsubscript{2} is probably due to the difference of the escape depth of the photoelectron between B 1s and Mg 2p, which is not considered here. That is, the elemental ratio of Mg and B for the dried supernatant estimated by XPS may also differ from the actual ratio (i.e., the amount of B is likely significantly underestimated by XPS). In any case, the nanosheets obtained as the dried supernatant of water with MgB\textsubscript{2} are composed of a boron framework as indicated by the presence of planar sp\textsuperscript{2}-bonded boron (Figure 2c) and possess a non-negligible amount of Mg as forms of oxidized magnesium, Mg(OH)\textsubscript{2} nanoparticles (Figure S4), and/or unreacted MgB\textsubscript{2} (as shown by ▼ in Figure 3a) as well as OH species. Here we note that unreacted MgB\textsubscript{2} was mostly found in the precipitate as indicated by the XRD pattern (Figure S3) while a small number of MgB\textsubscript{2} signals were detected from the dried supernatant by XRD (Figure 3a and Figure S2) which is probably due to the presence of unreacted MgB\textsubscript{2} left in the supernatant.

We consider that the exfoliation process of MgB\textsubscript{2} occurs while accompanying the proposed reaction i. Indeed, the complete ion-exchange between Mg cations and protons, leading to the formation of boron hydride (borophane) exfoliated nanosheets, can be achieved only by the ion-exchange method without using water (i.e., the exfoliation can be realized only by conducting reaction i while suppressing reaction ii). The complete ion-exchange between protons and Mg cations of MgB\textsubscript{2} will be reported elsewhere with detailed structure characterizations about the product of boron hydride sheets.\textsuperscript{15}

4. SUMMARY

We have investigated the mechanism of nanosheet formation by the reaction between MgB\textsubscript{2} and water. On the basis of the characterization of the reaction products and variations in pH and H\textsubscript{2} production with time after the mixing of MgB\textsubscript{2} and water, the essential reaction is considered to be an ion-exchange between protons and part of the Mg cations followed by the hydrolysis reaction between the Mg-deficient boron hydride sheets and water to produce H\textsubscript{2} and Mg-deficient hydroxyl-functionalized boron sheets. The nanosheets with a stacking periodicity of 0.70 nm can be obtained by drying the supernatant from the reaction of the water with MgB\textsubscript{2}, wherein the stacking sheets can be further exfoliated if the reaction was performed under ultrasonication. The nanosheets were found to be composed of a sp\textsuperscript{2}-bonded boron framework and possess a disordered structure, while the hydroxyl species and oxidized magnesium were uniformly distributed in the sheets.

ASSOCIATED CONTENT

\section{Supporting Information}

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b02348.

Materials, XRD patterns, and TEM images of the sheets or precipitate derived from m-MgB\textsubscript{2}, c-MgB\textsubscript{2}, or a-MgB\textsubscript{2} (PDF)

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