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Oriented Crystallization of Ammonium Sulfate from Hexagonal Boron Nitride/Sulfuric Acid Intercalation Compounds

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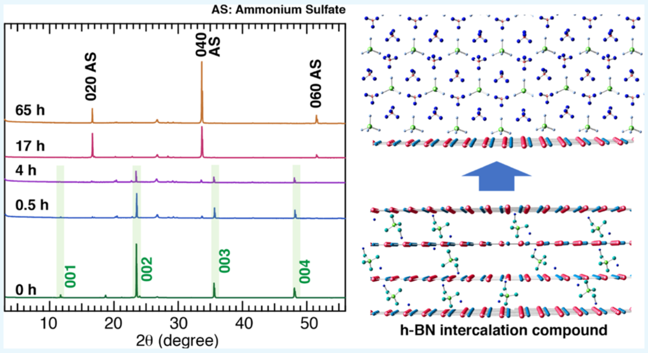
ABSTRACT: Controlling crystallization is a long-standing issue both from a fundamental and an applied perspective. In particular, our understanding of the influence of confinement on crystallization is far from complete. In this work, we utilize the confined interlayer spaces of hexagonal boron nitride (h-BN), which is one of the typical two-dimensional layered materials with atomically flat BN sheets, not only to prepare h-BN/H_2SO_4 intercalation compounds but also to initiate crystallization via the acid/base reaction between the intercalant (H_2SO_4) and gaseous ammonia. We report that the present acid/base reaction leads to the formation of highly oriented ammonium sulfate crystals along specific crystallographic directions. This oriented crystal growth originates from the 2D crystal nucleated in the confined interlayer spaces of h-BN.



■ INTRODUCTION

The idea of introducing foreign atoms, molecules, and ions into a two-dimensional solid lattice, that is, intercalation, provides an interesting strategy for the preparation of a variety of guest-host nanocomposite materials, such as graphite[1−3] and transition-metal dichalcogenide[4,5] intercalation compounds. A notable feature of the intercalation reaction is that the guest and host experience some degree of perturbation in their structural, mechanical, and electronic properties.[6,7] It has been documented that in intercalation compounds, the distance between two successive layers is a function not only of the intercalant composition[8] but also of the rigidity of the host layer against transverse distortion.[9] This implies that the in-plane arrangement of the intercalant within a given two-dimensional (2D) space is restricted by the compressibilities of the host layer. It is hence probable that 2D layered crystals and the related intercalation compounds open up new experimental possibilities for reaction and nucleation in confined environments.[10−12]

Motivated by the abovementioned consideration, we here investigate the intercalation and crystallization processes of the guest species in hexagonal boron nitride (h-BN), which is a structural analogue of graphite with a layered system of hexagonal lattices, each comprising covalently bonded boron and nitrogen atoms. Although the concurrent layers in h-BN are bound together by weak Van der Waals forces, the intralayer B−N bonds are extremely tough, leading to the structural anisotropy, inherent lubricity, and exceptional wear-resistant properties.[13−15] It has previously been recognized that the intercalation of h-BN is not performed easily but can be accomplished, for example, by the very strong oxidant $S_2O_6F_2$.[16] Recently, however, intercalation and the related exfoliation of h-BN have been shown to be possible using acid−base reactions[17−19] and sonication-assisted liquid-phase exfoliation.[20−22] Thus, h-BN intercalation compounds will offer an ideal and feasible experimental platform to investigate the possible effect of confined interlayer spaces on the structure and reactivity of the intercalant. In this work, we investigate the intercalation reaction of h-BN by a Brønsted acid H_2SO_4, which reaction was originally reported by Kovtyukhova et al.,[17] and then show how the interlayer spacing and its distribution is varied during aging in a dry environment at room temperature, eventually resulting in an almost pure phase of the h-BN/H_2SO_4 intercalation compound. We further demonstrate that the thus-obtained intercalated compound reacts with gaseous ammonium (NH_3), leading to oriented crystal growth of ammonium sulfate ($(NH_4)_2SO_4$) along specific crystallographic directions.

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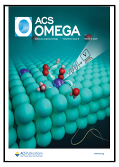

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■ RESULTS AND DISCUSSION

For the preparation of the intercalated h-BN/H_2SO_4 compounds, we first followed the reported methodology[17] in which H_2SO_4−h-BN suspensions drop-casted on a glass substrate are heated at 120−200 °C in air until the dried films are obtained (see the Experimental Section for details). This method yielded the dried sample with the X-ray diffraction (XRD) pattern characteristic to the intercalation compounds indeed, but the reproducibility was not perfect. Also, even if the intercalated phase becomes noticeable in the XRD pattern, diffraction peaks due to the original h-BN phase are still strong in intensity (Figure 1b), indicating that the resulting dried suspensions contain significant amounts of intact h-BN, as also pointed out in the literature.[17] We, however, found that aging of the dried suspensions at room temperature is quite effective and reproducible in developing the reflection pattern due to intercalated compounds. As shown in Figure 1c, when a heat-treated h-BN/H_2SO_4 sample with a little indication of intercalation in terms of XRD is stored at ambient temperature in a humidity-controlled chamber (relative humidity RH = 40 ± 1%) for several days, a set of 00*l* (*l* = 1, 2, 3, and 4) reflections with a *d* value of 7.4 Å (pattern I) is developed in a highly reproducible manner. Since the *d* value of the pattern I is more than the twice of the interlayer spacing of h-BN (*d* = 3.3 Å), this set of reflections demonstrates the formation of the stage-1 intercalation compound with a well-defined interlayer space. It should be reminded that these new reflections were developed when the as-heated h-BN/H_2SO_4 samples were aged under dry conditions at room temperature. This result suggests that guest molecules are already present in the interlayer spaces of the as-heat-treated sample irrespective of the absence of the characteristic reflection patterns of intercalation compounds. The subsequent dry-aging process will induce water desorption and the subsequent structural reorganization of H_2SO_4 molecules in the interlayer spaces to accommodate the dative interaction between the intercalant and the h-BN sheets,[17] resulting in a decrease in the spacing fluctuations. Thus, the initial heat-treated samples are likely to have the swollen structure[23,24] of irregularly stacked BN sheets, where all the interlayer spaces are filled sufficiently and randomly with H_2SO_4/H_2O molecules. Although the set of reflections of pattern I is stable as long as the samples are stored under controlled drying conditions, it can be replaced by another set of 00*l* reflections with a only slightly larger *d* value (*d* = 7.6 Å, pattern II) when they are exposed to ambient conditions for more than several months (Figure 1d). This suggests that the interlayer spacing will expand after prolonged air exposure due to water adsorption inside the h-BN matrix.

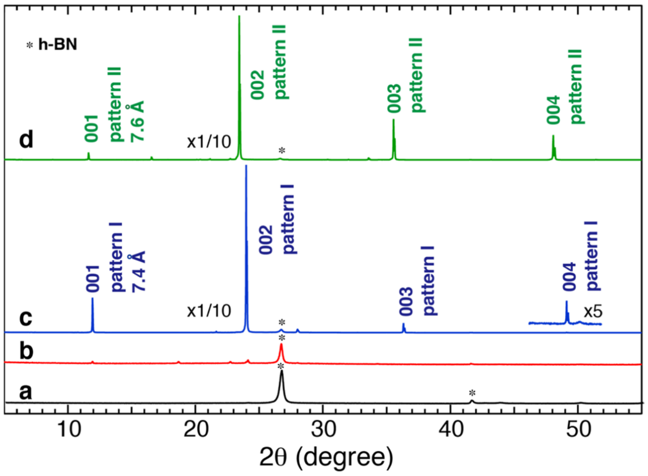

Figure 1. XRD patterns of (a) pristine h-BN powder and h-BN/H_2SO_4 films prepared by (b) heating the suspension at 170 °C for 38 h and then (c) storing at room temperature in a humidity-controlled chamber (RH = 40 ± 1%) for four days or (d) exposing to ambient conditions for more than six months. The inset shows a magnified plot of (c) in the 2*θ* range from 46 to 52°. The asterisk (*) indicates the h-BN reflections.

To get further knowledge about the structural properties of the h-BN/H_2SO_4 samples, we performed infrared measurements using attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy (Figure 2). As shown in the left panel of Figure 2, the FTIR spectrum of the as-heated h-BN/H_2SO_4 films (Figure 2b), which have no characteristics of intercalated phases in terms of XRD (see Figure 1b), and those of the patterns I (Figure 2c) and II (Figure 2d) intercalation compounds illustrate several maxima in the 2800−3400 cm^{-1} range, which are assigned to less-polarizable H bonds within the interlayer spaces in h-BN.[17] This allows us to assure that even in the as-heated h-BN/H_2SO_4 films, sulfuric acid is incorporated into the interlayer spaces although the sample does not exhibit 00*l* Bragg reflections. In the left panel of Figure 2b, one also notices a broad band centered at ~1700 cm^{-1}, which can be assigned to the superimposed $\delta(H_2O)$ and $\delta(H_3O^+)$ mode.[17,25] These observations imply that the as-heated h-BN/H_2SO_4 films can be regarded as swollen samples, as mentioned earlier. In the FTIR spectrum of the pattern I intercalation compound shown in Figure 2c, however, a broad band at ~1700 cm^{-1} is almost missing, indicating that most of the water molecules in the as-heated h-BN/H_2SO_4 film are desorbed during the post-drying process. In the FTIR spectrum of the pattern II intercalation compound shown in

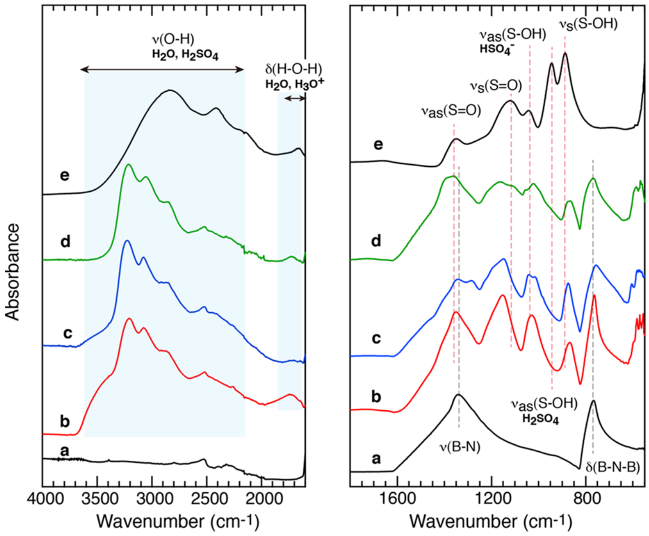

Figure 2. ATR-FTIR spectra of (a) pristine h-BN powders and h-BN/H_2SO_4 films prepared by (b) heating the suspension at 170 °C for 38 h and then (c) storing at room temperature in a humidity-controlled chamber (RH = 40 ± 1%) for four days (pattern I intercalation compound) or (d) exposing to ambient conditions for more than six months (pattern II intercalation compound). ATR-FTIR spectrum of (e) H_2SO_4 liquid is also shown for comparison.

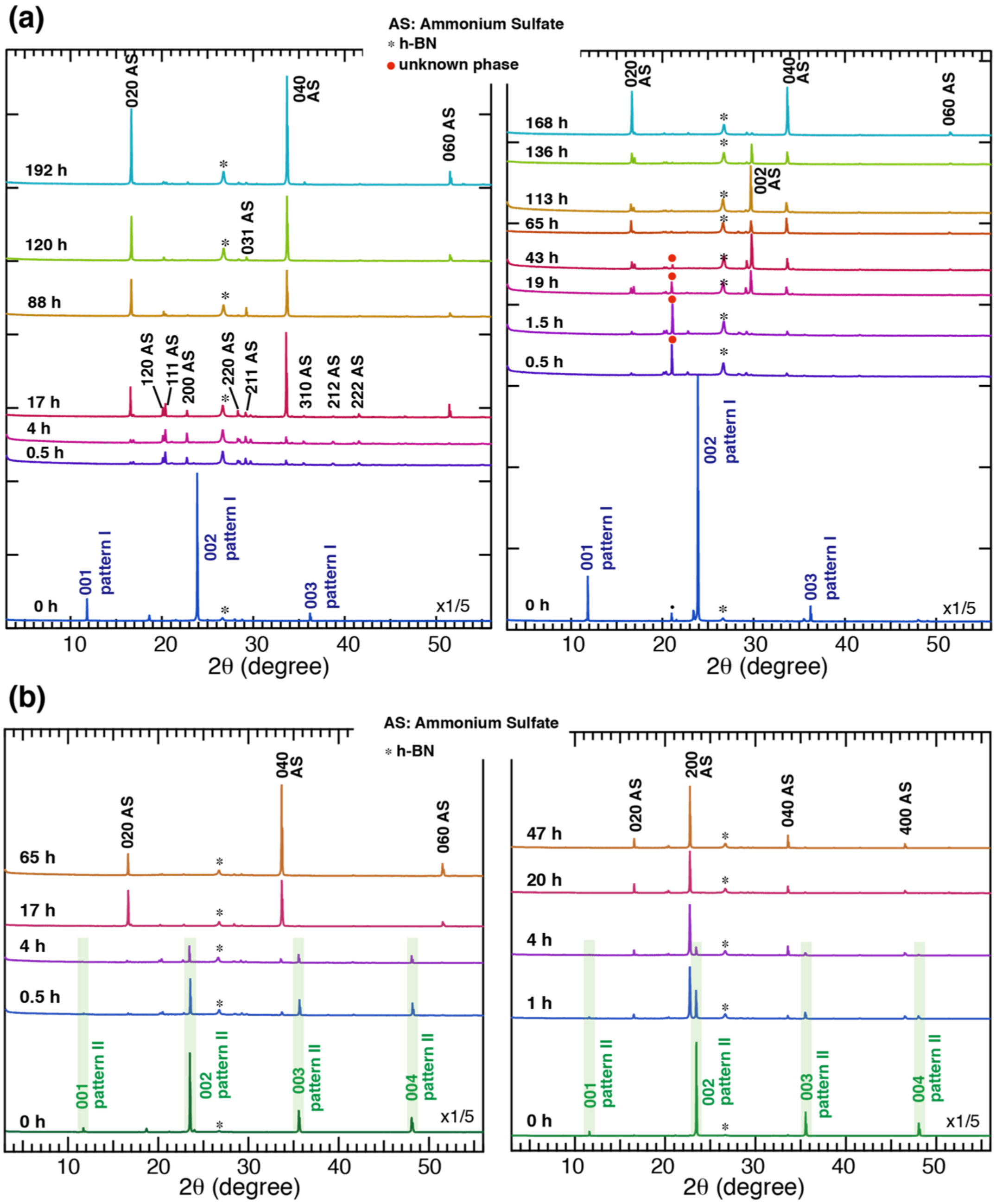

Figure 3. Changes in the XRD pattern of two different h-BN/H_2SO_4 intercalation compounds with (a) pattern I and (b) pattern II after the reaction with gaseous NH_3 for different reaction times (indicated in the graphs). The asterisk (*) represents the h-BN 002 reflection.

Figure 2d, a broad band peaking at ∼1700 cm^{-1} is partially retrieved. This provides a signature of water adsorption after a long-term air exposure, as also noted earlier.

The right panel in Figure 2 shows the IR spectra in the wavenumber region below 1800 cm^{-1}. In agreement with the previous literature,[17] the $\nu_{as(S-OH)}$ band of H_2SO_4 ($\nu \sim 950$ cm^{-1}) disappears and that of the HSO_4^- anion ($\nu \sim 1050$ cm^{-1}) increases in intensity, suggesting substantial dissociation of H_2SO_4 into HSO_4^- and H^+. The resulting HSO_4^- ions will lead to the formation of strong dative bonds between HSO_4^- and B of the BN layer ($>S{=}O: \rightarrow B^{\delta+}$), whereas H^+ ions will protonate the nitrogen.[17] Hence, the driving force for the insertion of H_2SO_4 into h-BN would be the strong electron-donating behavior of sulfuryl groups along with the protonation characteristics of BN layers, as has been proposed in the literature.[17] Thus, it can be said that the present intercalation is thermodynamically driven, which eventually leads to swelling of the galleries, as observed during polymer intercalation of layered silicates.[26] This consideration will not only account for the formation of the swollen structures but also explain the reason why in h-BN/H_2SO_4 intercalation compounds, one does not observe 00*l* reflections characteristic to higher stages,[17] such as stages 2 and 3, which are typical products of graphite intercalation with oxidizing agents.

Thus, since we have obtained highly reproducible, robust, and pure h-BN/H_2SO_4 intercalation compounds, these samples can be used to induce a chemical reaction within the 2D confined space. For this purpose, we utilize the acid/base reaction between the intercalant (H_2SO_4) and gaseous NH_3. If this acid/base reaction occurs successfully, it should

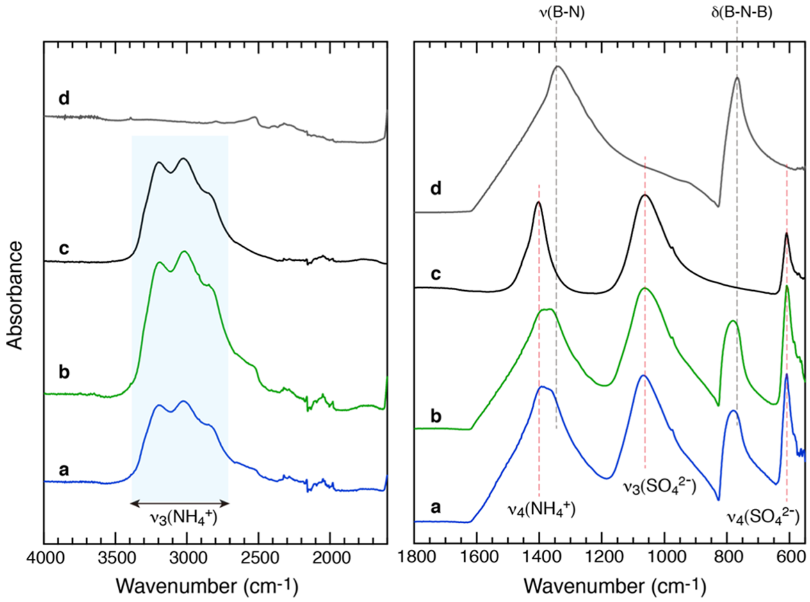

Figure 4. ATR-FTIR spectra of h-BN/H_2SO_4 intercalation compounds with (a) pattern I and (b) pattern II after the reaction with gaseous NH_3 for 73 h. ATR-FTIR spectra of (c) $(NH_4)_2SO_4$ and (d) h-BN powders are also shown for comparison.

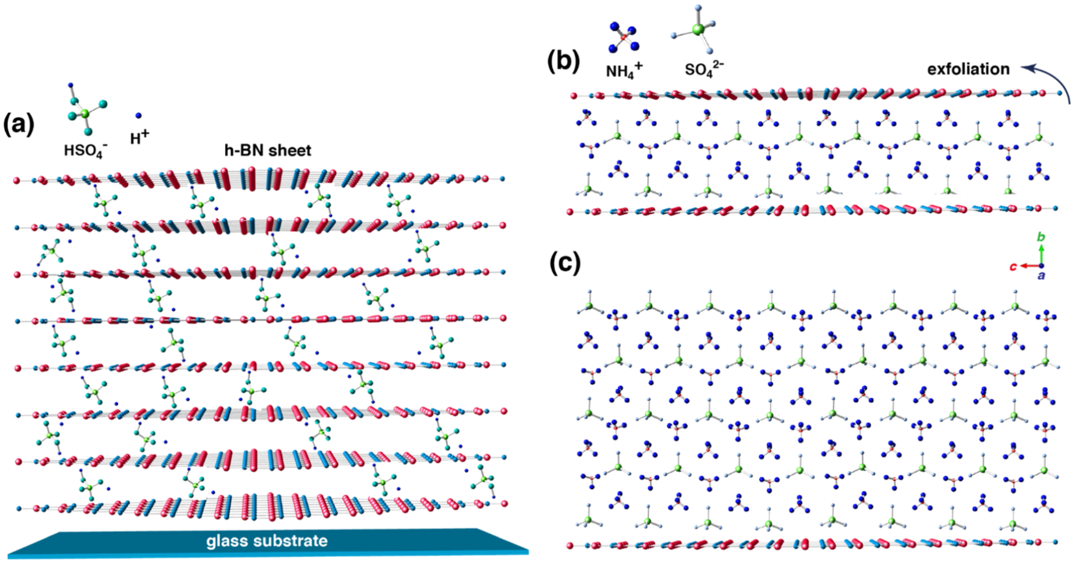

Figure 5. Schematic representation of the h-BN/H_2SO_4 intercalation compound on a glass substrate (a) before and (b,c) after the reaction with gaseous NH_3. In (a), sulfuric acid is supposed to be dissociated into HSO_4^- and H^+ ions, accompanied by possible partial protonation of the nitrogen atoms of BN.[17] (b) Expected structure of the 2D $(NH_4)_2SO_4$ crystal layer created in the confined interlayer space, followed by exfoliation of the top h-BN sheet. (c) Oriented aggregation of ammonium sulfate molecules on the 2D crystal layer, forming an iso-oriented bulk crystal.

result in ammonium sulfate $(NH_4)_2SO_4$, which has an orthorhombic structure (*Pnam*) with four formula units per unit cell comprising three ionic groups.[27] In order to achieve the expected acid/base reaction under ammonia vapor, the h-BN/H_2SO_4 intercalation compounds were held in a sealed container at room temperature together separately with ammonia solution in an alumina crucible (for details, see the Experimental Section). Figure 3 shows examples of the XRD patterns obtained from different intercalated samples, which originally have the 00*l* reflections characteristic of pattern I (Figure 3a) and II (Figure 3b) intercalation. During the first 1 h of reaction time, the set of 00*l* reflections characteristic of intercalation shows a substantial decrease in intensity, implying the development of an exfoliated structure due to the expected gas-phase acid/base reaction. In concomitant with the decrease in the intercalation reflections, other sets of diffraction peaks increase in intensity with increasing reaction time. Although the relative intensity ratio of these newly emerged peaks varies from sample-to-sample, their positions match exactly with those of $(NH_4)_2SO_4$,[27] which is the product we expected. Also, we confirmed from the ATR-FTIR measurements that the thus-prepared product can be interpreted as due to the combination of $(NH_4)_2SO_4$ and h-BN (Figure 4). From these results, we can conclude that the resulting compounds consist of $(NH_4)_2SO_4$ and (partially exfoliated) h-BN sheets. It should also be worth mentioning that in the XRD patterns of the reaction products, the *h*00 and/or 0*k*0 reflections of $(NH_4)_2SO_4$ are developed for all the samples investigated, implying highly oriented crystallization along *a*- and/or *b*-axes during the present acid/base reaction. In this work, we prepared the h-BN/H_2SO_4 intercalation compounds by drop-casting the h-BN/H_2SO_4 suspension on a glass substrate. Hence, it is likely that the resulting intercalated layered compounds and the initial h-BN layers are mostly stacked in parallel with a surface of the glass substrate (Figure 5a). Such a horizontally stacked configuration is presumably responsible for the detection of the preferred orientation growth of $(NH_4)_2SO_4$ as each basal BN layer can behave as a good substrate for the crystal growth of $(NH_4)_2SO_4$. However, this will not simply guarantee the oriented crystal growth because the structures of h-BN and $(NH_4)_2SO_4$ are crystallographically quite different; the former and the latter have hexagonal and orthorhombic unit cells, respectively. Thus, the possibility of an epitaxial growth of $(NH_4)_2SO_4$ on an h-BN sheet should be excluded. Rather, we suggest that the spatially confined interlayer spaces inherent to the h-BN intercalation compounds provide an opportunity to initiate the formation of well-structured single crystals in 2D (Figure 5b). Once such 2D $(NH_4)_2SO_4$ crystals are formed in the interlayer spaces, the dative chemical bonding between the original intercalant (H_2SO_4) and the BN sheets will be missing, which eventually leads to the exfoliation of BN sheets (see also Figure 5b). Then, the resulting 2D $(NH_4)_2SO_4$ crystals will act as an ideal "substrate" for the subsequent "homoepitaxial" crystal growth (Figure 5c). This is analogous to the case of prenucleation layers that are created adjacent to the atomically smooth solid surface under confinement conditions.[12,28,29] The final growth orientation will be governed by the crystallographic direction of the basal crystal structure, which will be determined by the configuration and bonding environment of the intercalation species. It is probable that the structural environment of the intercalants is not uniform throughout the interlayer spaces. This will account for the variation of the preferred crystal growth direction of $(NH_4)_2SO_4$, as shown in Figure 3. Although a full control of the crystal growth direction is a problem that needs to be solved, we suggest that the present method of oriented crystal growth can be basically extended to other 2D materials, for example, graphite, which can also encapsulate acid molecules within the interlayer spaces.[18] Furthermore, the expected increase in the basal spacing reduces the interlayer cohesive energy, which facilitates exfoliation to atomic layers.[18,19,30] Thus, the oriented crystal growth initiated by the formation of ultrathin crystalline layers in the 2D galleries will provide a new possibility of 2D materials in terms not only of crystallization in confinement but also of exfoliation in dry environments.

■ CONCLUSIONS

We have shown that appropriate heating of the h-BN/H_2SO_4 suspensions can lead to a swollen phase, in which all the interlayer spaces are filled with H_2SO_4/H_2O molecules to yield random spacing between the adjacent BN layers. When the swollen sample is aged under dry conditions, most of the water molecules are desorbed to form intercalation compounds with a well-defined interlayer spacing. The acid/base reaction between the intercalation compound and gaseous NH_3 leads to the formation of the 2D $(NH_4)_2SO_4$ crystal in the confined interlayer spaces of h-BN, which eventually leads to highly oriented crystal growth along specific crystallographic orientations.

■ EXPERIMENTAL SECTION

Materials. Boron nitride was purchased from Aldrich (purity ~98%, particle size ~1 μm) without any additional treatment. We confirmed that the sample powders show Bragg X-ray diffraction peaks attributed only to the h-BN phase. Sulfuric acid (95%) was obtained from Wako Pure Chemical Industries, Ltd. and was used as purchased.

Synthesis of h-BN/H_2SO_4 Intercalation Compounds. We prepared h-BN/H_2SO_4 intercalation compounds basically according to the procedure reported in the literature.[1] A 30 mg amount of h-BN was added to 0.5 mL of sulfuric acid in a glass vial and stirred with a glass stick. A drop of the thick h-BN/H_2SO_4 suspension was cast on a glass substrate (18 × 18 × 0.13 mm). The wet samples were heated in air at a temperature of 170 °C in a drying oven. After the heating time of 30−50 h, dried films with a light-gray color were obtained. The dried films were stored in a humidity-controlled chamber with a relative humidity of 40 ± 1% at ~20 °C. Some of the aged samples were then exposed to ambient conditions.

Reaction of h-BN/H_2SO_4 Intercalation Compounds with Gaseous Ammonia. The ammonia solution was obtained from Wako Pure Chemical Industries, Ltd. as a saturated aqueous solution (~30 wt %). To induce the acid/base reaction between the h-BN/H_2SO_4 intercalation compounds with gaseous NH_3, we put the intercalation compounds formed on a glass substrate in a sealed container at room temperature together separately with the ammonia solution in an alumina crucible. After the appropriate reaction times, the sample was taken out from the container and was used for characterization.

Characterization. The structure of these film samples on a glass substrate was characterized by X-ray diffraction (XRD) with a diffractometer (SmartLab, Rigaku) using Cu Kα radiation. ATR-FTIR spectra were also collected with an FTIR spectrometer (Nicolet Is5, Thermo Fisher Scientific).

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Notes

The authors declare no competing financial interest.

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