

Study on Swelling Behavior of Layered Perovskite Niobate and its Exfoliation Process toward the Synthesis
of High-quality Nanosheets
(高品位ナノシート合成に向けた層状ペロブスカイトニオブ酸化物の膨潤・剥離挙動に関する研究)

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1. Introduction

The swelling and exfoliation behaviors of layered perovskite niobate single crystals using various organo-ammonium ions are described herein. Metal oxide nanosheets have received tremendous attention due to their intriguing chemical and physical properties originating from their two-dimensional (2D) nature with molecular thickness. Two-dimensional nanosheets, such as graphene, are expected to be utilized in a range of fields, particularly in the field of nanoelectronics. In particular, oxide nanosheets exhibit dielectric and insulating properties with high chemical and thermal stability, which are useful in a wide range of applications, such as high-k capacitor devices. However, to exploit nanosheets for practical use, control over the size and shape of the nanosheets becomes important, because these factors significantly affect their performances. For example, thin films composed of small nanosheets inevitably have many boundaries and gaps, which lead to current leakage and reduced dielectric response, indicating that nanosheets with small lateral dimensions are not suitable for some practical applications. Therefore, the controlled synthesis of nanosheets with large lateral dimensions is important for improving device performance. However, adequate attention has not been paid to this issue so far.

Several routes have been developed to produce 2D nanosheets via disintegration of layered compounds. Mechanical cleavage using Scotch tape is the most straightforward method to produce nanosheets from host crystals, though there are some drawbacks, such as low reproducibility and low yield. The other commonly used technique to yield nanosheets is ultrasonication in a solvent, which is still limited by low yield of unilamellar sheets accompanied by a large number of thicker fragments. Furthermore, these methods can be applied only to van der Waals layered compounds, such as layered metal dichalcogenides and graphite, which are recognized to have rather weaker layer-to-layer interactions. Thus, compounds such as clay minerals, and layered oxides and hydroxides cannot be exfoliated through these techniques due to the strong attraction force between layers. Instead, these compounds possess ion-exchange properties, and exfoliation based on their

chemical reactivity is suggested. It has been reported that layered metal oxide crystals and clay minerals show large osmotic swelling in aqueous solutions containing alkali metal ions and organoammonium ions, which leads to facile delamination into nanosheets. Exfoliation through osmotic swelling is known to produce nanosheets of large lateral size in high yield. For example, some layered oxide compounds exhibit a large extent of osmotic swelling upon inclusion of a large quantity of electrolytic solution, which results in expansion of the interlayer gallery, drastically weakening the cohesive force between neighboring layers. Consequently, this swelling phenomenon facilitates the disintegration of the layered crystals into its elementary layers. Although the production of nanosheets through osmotic swelling has been realized for many layered materials, studies that focus on swelling as a key intermediate step of exfoliation are relatively rare and limited to only a few examples, such as clay minerals and layered titanates.

Studies on osmotic swelling and exfoliation have been carried out mainly using polycrystalline powder samples. This limits our understanding because of the small crystallite size, which hampers stable swelling. Only recently have monodisperse single-crystal samples with a size of several tens of micrometers been employed in swelling studies, which enable not only the direct observation of the extensive degree of swelling but the size and shape-controlled synthesis of high-quality nanosheets. Systematic studies using single crystals can yield important information about the swelling and exfoliation mechanism of layered materials, as well as lead to the tailored synthesis of nanosheets. However, examples are limited to layered titanates and fluorohectrite crystals. Therefore, it is essential to examine the osmotic swelling and exfoliation behaviors of other layered materials with different crystal structures and chemical compositions.

Perovskite-type oxide nanosheets, such as $\text{Ca}_2\text{Nb}_3\text{O}_{10}^-$, can be obtained via delamination of their parent layered Dion-Jacobson-type perovskite, $\text{KC}_2\text{Nb}_3\text{O}_{10}$. Calcium niobate nanosheets, along with their precursor layered forms, have attracted increasing interest in recent decades due to their fascinating properties, including high-k dielectricity, photocatalytic activity, and ion-exchange properties. These properties allow their potential use in the fields of electronics, catalysis, and intercalation chemistry. For these reasons, it is of great importance to explore the swelling and exfoliation behaviors of layered perovskite oxide crystals and thus to produce high-quality perovskite nanosheets. In this study, we systematically investigated the swelling behavior of $\text{HCa}_2\text{Nb}_3\text{O}_{10} \cdot 1.5\text{H}_2\text{O}$ in its single-crystal form using various intercalants and revealed their influence on the exfoliation mechanism.

For the exfoliation of layered metal oxides, quaternary ammonium hydroxides, such as tetraalkylammonium hydroxide (TAAOH), are generally employed as swelling/exfoliation reagents. In particular, tetrabutylammonium (TBA) is widely used. The extent of swelling of the layered crystals is known to be governed by the equilibrium of the osmotic pressure rather than the identity of the intercalant. However, the structure and chemical composition of the compound will affect the swelling behavior. Moreover, the influence of the swelling reagent on the exfoliation behavior is not fully understood, although some reports have demonstrated that guest ions incorporated into the gallery significantly impact the lateral size of the nanosheets and the degree of disintegration of the swollen crystals. It is assumed that the exfoliation behavior can be determined by the size and polarity of the intercalated guest ions. The fundamental understanding of

how swelling species affect the exfoliation process is imperative for achieving the controlled synthesis of high-quality 2D nanosheets, as well as obtaining deep insight into the swelling and exfoliation of inorganic layered materials in general.

In this study, the osmotic swelling and the exfoliation behavior of a typical layered oxide compound, $\text{KCa}_2\text{Nb}_3\text{O}_{10}$, were systematically examined using various organoammonium bases. This thesis study was carried out in the following three parts:

(1) Swelling reaction of layered perovskite niobate crystals, $\text{HCa}_2\text{Nb}_3\text{O}_{10} \cdot 1.5\text{H}_2\text{O}$, with various tetraalkylammonium hydroxides

(2) Exfoliation behavior of $\text{HCa}_2\text{Nb}_3\text{O}_{10} \cdot 1.5\text{H}_2\text{O}$: Stability (or ease of exfoliation) of the swollen samples and lateral dimensions of the exfoliated nanosheets

(3) Investigation of the origin of nanosheet fragmentation and high-quality production

2. Swelling reaction of layered perovskite niobate crystals, $\text{HCa}_2\text{Nb}_3\text{O}_{10} \cdot 1.5\text{H}_2\text{O}$, with various tetraalkylammonium hydroxides

Impurity-free single crystals of $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ were synthesized through flux-mediated growth and subsequently converted into $\text{HCa}_2\text{Nb}_3\text{O}_{10} \cdot 1.5\text{H}_2\text{O}$ through an acid-exchange process. The fraction of platelet crystals in the size range of 25-53 μm was used in the swelling/exfoliation studies. The crystal thickness was approximately 5-20 μm , which corresponds to a stack of 3000-12000 layers, considering the basal spacing of 1.63 nm.

The obtained $\text{HCa}_2\text{Nb}_3\text{O}_{10} \cdot 1.5\text{H}_2\text{O}$ crystals were immersed in four kinds of TAAOH solutions (TMA, TEA, TPA, and TBA, where M, E, P, and B indicate methyl-, ethyl-, propyl-, and butyl group). The concentrations of the solutions were varied from $\text{TAA}/\text{H}^+ = 0.1$ to 10, corresponding to the TAA dose needed to equal 0.1 to 10 folds the exchangeable protons in the crystals. A batch of TBAOH samples are shown here as a representative of the other TAA samples. The platelet crystals showed noticeable uniaxial elongation along the stacking direction of the host layers (**Figure 1a**, right panel), which is in sharp contrast to the crystals before the reaction (**Figure 1a**, left panel). After equilibration in each concentration, the samples exhibited significant volume expansion, observed at the bottom of the graduated cylinder (**Figure 1b**). The crystal volume increased with increasing TBA^+ dose, showing a maximum at $\text{TBA}^+/\text{H}^+ = 0.3$, and then gradually decreased at higher TBAOH concentrations. Small-angle X-ray scattering (SAXS) revealed that the swollen crystals had interlayer spacings in the range of 22 nm to over 100 nm depending on the solution concentration (**Figure 1c**). The change in basal spacing at varied solution concentration agreed well with the change in sample volume. Therefore, both the large elongation of the crystals and the volume expansion can be explained by the homogeneous interlayer expansion of interlayer spacing *via* introduction of a large volume water and TBA ions. On the other hand, the number of TBA ions incorporated into $\text{HCa}_2\text{Nb}_3\text{O}_{10} \cdot 1.5\text{H}_2\text{O}$ was estimated by determining the concentration of the solutions *via* acid-base titration before and after the reaction. The uptake rapidly increased with the initial TBA^+ dose up to $\text{TBA}^+/\text{H}^+ = 0.5$, where over 90 % of the applied

TBA⁺ was taken up into the crystals, leaving the ion concentration outside the crystals nearly zero. When TBA⁺/H⁺ > 0.5, the uptake reached saturation at a value corresponding to the replacement of ~40 % of the H⁺ in the crystal, and the concentration of TBA⁺ in the solution increased accordingly. The saturation uptake of 40 % can be ascribed to steric effects, which limit further intercalation of the ions. Therefore, the suppression of the interlayer spacing at higher solution concentrations can be understood by the osmotic pressure outside of the crystals associated with an increase in the TBAOH concentration. The samples reacted with the other TAA solutions, *i.e.*, TMA, TEA, and TPA, showed a similar trend in the swollen volume against their concentrations except for minor differences. The swelling reaction started at the lowest dose of reagents, TAA⁺/H⁺ = 0.1, and the expansion was enhanced up to a point, TAA⁺/H⁺ = 0.4 ~ 0.5 and 0.2 ~ 0.3 for TMA and TEA and for TPA and TBA, respectively, to reach the maximum volume. Beyond the maximum expansion, the volume gradually decreased with an increase in the solution concentration. In contrast, the saturation amount of guest ions was increased up to ~ 60 % (for TMA) with the decrease in ion size. The reduction in uptake from TMA to TBA can be reasonably ascribed to the difference in the size of the TAA ion. TAA ions accommodated in the largely expanded oxide galleries are assumed to be distributed from the Stern layer to the diffuse layer. Considering the energy gain through strong electrostatic interactions, it is reasonable to assume that a majority of counter ions reside in the vicinity of the host layers and a minor amount of ions gradually diffuse into the interlayer space. Based on this assumption, the packing density of TAA ions on the oxide layer can be estimated to be approximately 54 % and 71 % for TMA and TEA and 103 % and 140 % for TPA and TBA, which indicates that the rather bulky ions are closely associated or interdigitated, while smaller ions are isolated.

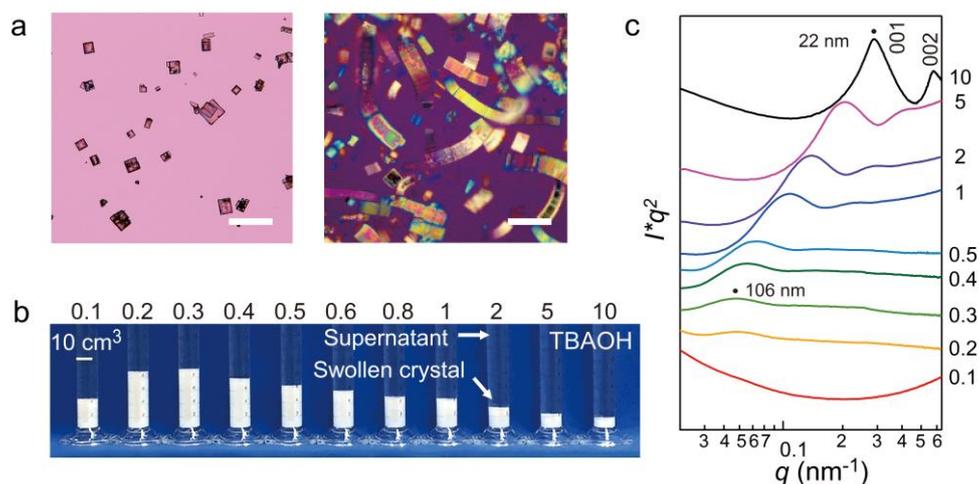


Figure 1. (a) Polarized optical microscopy images of the platelet crystals of $\text{HCa}_2\text{Nb}_3\text{O}_{10} \cdot 1.5\text{H}_2\text{O}$ before (left) and after swelling (right) in TBAOH solution. The crystals lie down, having their basal and side planes parallel to the sample stage before and after the reaction, respectively. (b) Photograph of 0.2 g of $\text{HCa}_2\text{Nb}_3\text{O}_{10} \cdot 1.5\text{H}_2\text{O}$ swollen in 25 cm³ of aqueous solution of TBAOH at various concentrations. (c) SAXS data of the swollen crystals in TBAOH solution at various concentrations. Scale bars are 100 μm. The numbers in (b) and (c) represent N^+/H^+ .

3. Exfoliation behavior of $\text{HCa}_2\text{Nb}_3\text{O}_{10} \cdot 1.5\text{H}_2\text{O}$: Stability (or ease of exfoliation) of the swollen samples and lateral dimensions of the exfoliated nanosheets

To understand an impact of the intercalant on the exfoliation behavior, the exfoliation behavior in the four different TAAOH solutions was examined. The extent of swelling of the crystals with the different guest species was compared at the same solution concentration of $\text{TAA}^+/\text{H}^+ = 1$. At this concentration, the interlayer distance was in the range of 56-63 nm, indicating that the degree of swelling is comparable for each specimen.

We examined the exfoliation of the swollen crystals and compared the quality of the obtained nanosheets after mechanical shaking for one day. The representative atomic force microscopy (AFM) images in **Figure 2a** show that the nanosheets obtained from the swollen crystals have a unique thickness of 1.80 nm. This value is consistent with the previously reported thickness of unilamellar $\text{Ca}_2\text{Nb}_3\text{O}_{10}^-$ nanosheets. In contrast, the lateral size of the nanosheets was strongly dependent on the reagents; the nanosheets produced with TMA and TEA solutions exhibited a large lateral width of 8 μm on average, while delamination with TPA and TBA, which have longer alkyl chains, involved fragmentation, resulting in nanosheets with a much smaller lateral size (~ 400 nm).

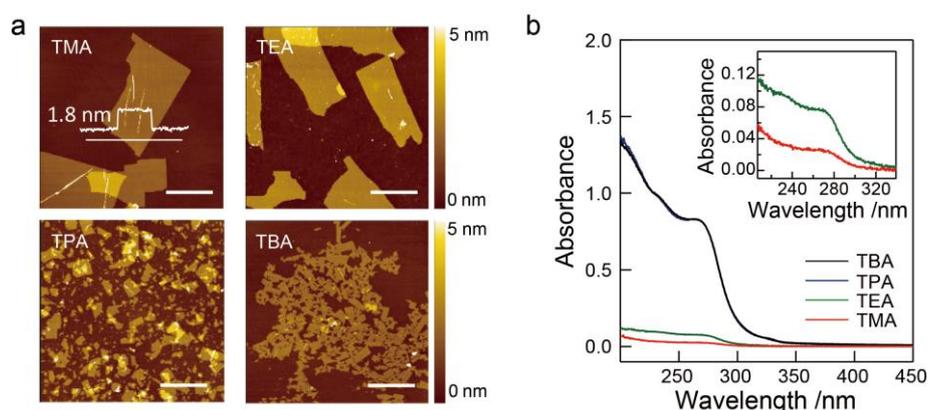


Figure 2. (a) AFM images of the $\text{Ca}_2\text{Nb}_3\text{O}_{10}^-$ nanosheets obtained by TMAOH, TEAOH, TPAOH, and TBAOH. (b) UV-visible absorption spectra of the $\text{Ca}_2\text{Nb}_3\text{O}_{10}^-$ nanosheet suspensions. An aliquot of each suspension was pipetted, diluted to one hundredth of its original concentration with water and subjected to measurement. The inset shows the magnified spectra to emphasize the absorption intensities of the TMA and TEA samples.

Because nanosheet suspensions show intense optical absorption, the UV-visible absorption spectra of the colloidal nanosheets were measured to estimate the exfoliation yields for the samples with the four TAA ions. As shown in **Figure 2b**, a noticeable difference in absorbance was observed between two groups: Group 1 (TMA and TEA) showed very low absorbance, while Group 2 (TPA and TBA) showed a much higher absorbance. The absorption at 265 nm was converted to the exfoliation yield using the experimentally determined molar extinction coefficient ($\epsilon = 2.46 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), which indicated that the extent of

exfoliation of the TPA and TBA samples (Group 2) was 92 % after one day of mechanical shaking. In contrast, the yield for the TMA and TEA samples (Group 1) was only 3 % and 9 %, respectively. Unexfoliated samples in Group 1 were observed under polarized optical microscopy, which indicated that the residue retained the swollen structure with shortened crystal lengths.

In summary, nanosheets with large lateral dimensions can be obtained by using aqueous solutions of smaller ions, *i.e.*, TMA and TEA, without severe fragmentation but in limited yields. These results suggest that crystals swollen with smaller hydrophilic ions are rather stable in aqueous media. On the other hand, the crystals swollen in TPA and TBA solutions showed an extensive degree of delamination (>90 %), and the obtained nanosheets were substantially fragmented.

4. Investigation of the origin of nanosheet fragmentation and high-quality production

As noted above, exfoliation with bulky ions such as TPA and TBA induced significant fragmentation of the nanosheets, while smaller ions (TMA and TEA) yielded large, well-defined nanosheets. There are two possible explanations to describe the fragmentation that occurs during exfoliation by the bulky TPA and TBA. 1) Mechanical stress imposed on the host layers in the initial stage of intercalation of these bulky ions may damage the oxide layers. As a consequence, the nanosheets are broken into small pieces when an external shear force is applied. Although a well-expanded structure resulted upon equilibration with the TAA solutions, it is expected that stress from large guests will be greater than that from small ones because reaction is initiated by the penetration of guests into the narrow interlayer gallery (which has a height of 1.63 nm, as determined by XRD) of $\text{HCa}_2\text{Nb}_3\text{O}_{10} \cdot 1.5\text{H}_2\text{O}$. 2) The intrinsic properties of the guest species, especially the hydrophobicity, may be associated with the exfoliation behaviors of the layered compounds. Bulky ions may be interdigitated with each other, while smaller ions are isolated. Thus, the intermolecular hydrophobic interactions should be stronger for TPA and TBA ions in aqueous media, which may impose some mechanical stress on the oxide nanosheets. The following verification procedures were performed to test these hypotheses.

4.1. Verification of hypothesis 1: Guest ion replacement of TMA with TBA

We carried out the following experiments, to consider involvement of mechanical stress in the initial stage of intercalation as a possibility for lateral fracture. The large nanosheets (~8 μm) obtained by TMAOH were brought into contact with TBAOH solution by replacing TMA ions. Then, we monitored the lateral size change to determine the effect of TBA ions on the size of the nanosheets. The suspension containing nanosheets with large dimensions was centrifuged and dispersed into the TBAOH solution to promote the replacement of TMA with TBA ions. The extent of ion exchange was estimated from the *d*-spacing of the restacked nanosheets, as the *d*-spacing of the compound is dependent on the size of the interlayer guests. The restacked sample prepared through this solution replacement yielded a *d*-value of 2.50 nm, as shown in **Figure 3a**. This value is much closer to that of the sample exposed to the TBA solution, proving the substantial replacement of TMA with TBA. Significant fragmentation was observed particularly with mechanical shaking. After 24 hours of shaking, the size of the nanosheets became small (**Figure 3c**), and the degree of fragmentation was similar to that from

direct exfoliation in TBAOH solution. Therefore, we can reasonably assume that the fragmentation of nanosheets shown in this experiment cannot be supported by hypothesis 1, because this experiment was designed to exclude mechanical stress on the layers upon the introduction of TBA ion. To confirm the impact of the treatment in this experiment (centrifugation and dispersion) and mechanical shaking on the lateral size of the nanosheets, a control experiment was performed. The control sample was prepared by replacing the supernatant with TMAOH solution instead of TBAOH solution. Interestingly, a change in the lateral size was not observed in this control sample even after shaking. This proves that the 24 hours of shaking is not responsible for the fragmentation. Consequently, the results support that neither the mechanical stress caused by the intercalation of bulky ions nor strong shaking is the origin of the lateral fragmentation of the nanosheets.

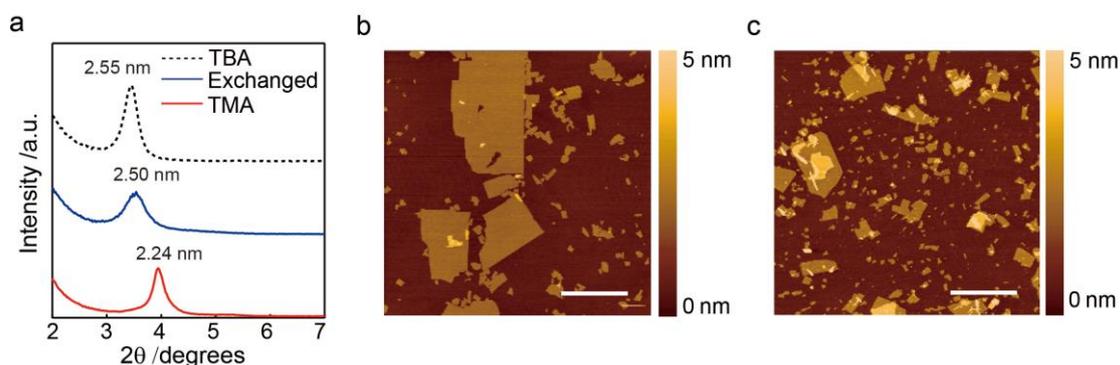


Figure 3. (a) XRD patterns of restacked nanosheets obtained in TBAOH and TMAOH solutions and after solution exchange. For the restacking, several drops of the suspension were dried on a glass slide in N_2 atmosphere. XRD data were collected under N_2 gas flow. AFM images of TMA-to-TBA ion-exchanged nanosheets (b) before and (c) after the mechanical shaking. Scale bars on the AFM images are 5 μm .

4.2. Verification of hypothesis 2: Suppression of hydrophobic interaction using organic solvent

The fragmentation of nanosheets in the presence of bulky ions may be caused by interaction among the ions, for example, hydrophobic interaction. Based on our hypothesis, we tried to attenuate the intermolecular interaction between TBA ions by exchanging the aqueous medium with other organic solvents. After swelling the crystals in an aqueous solution of TBAOH, the supernatant was decanted, and methanol (CH_3OH) or dimethyl sulfoxide (DMSO) was added. This replacement was repeated 5 times to ensure complete solvent exchange. The crystals in each solution were still characterized as having a swollen structure and maintained a large interlayer distance. After 24 hours of mechanical shaking of such swollen crystals, the nanosheets in each solvent were not broken into small pieces, which is in sharp contrast to the samples in aqueous solution. The lateral fracture was effectively suppressed in organic solvents. The average lateral sizes of the obtained nanosheets were approximately 6 μm and 10 μm in CH_3OH and DMSO, respectively, as shown in the AFM images (**Figure 4a and b**). In addition to the large lateral size, the nanosheets were rather regularly shaped with sharp facets derived from the original platelet crystals. This result clearly indicates the much lower degree of lateral fracture and supports our idea that the intermolecular hydrophobic interaction promotes fragmentation of the nanosheets.

The UV-vis spectrum of the CH₃OH suspension (**Figure 4c**) revealed a very low concentration of nanosheets, which contrasts the concentration in H₂O, while DMSO gave relatively a higher concentration, corresponding to 24 % of exfoliation yield.

The verification of hypothesis 2 shows that the chemical interaction associated with the hydrophobicity of the intercalants is exerted among the bulky ions and results in fragmentation in aqueous solution. Such intermolecular interactions can be successfully suppressed and controlled by changing the medium to organic solvents. Hence, we propose the following mechanism of fragmentation. The bulky ions adsorbed to the oxide layer are closely associated with each other due to hydrophobic intermolecular interactions, which may result in distortion or deformation of the nanosheets, especially when a shear force is applied. Vigorous bending of the nanosheets induced by shaking leads to fragmentation.

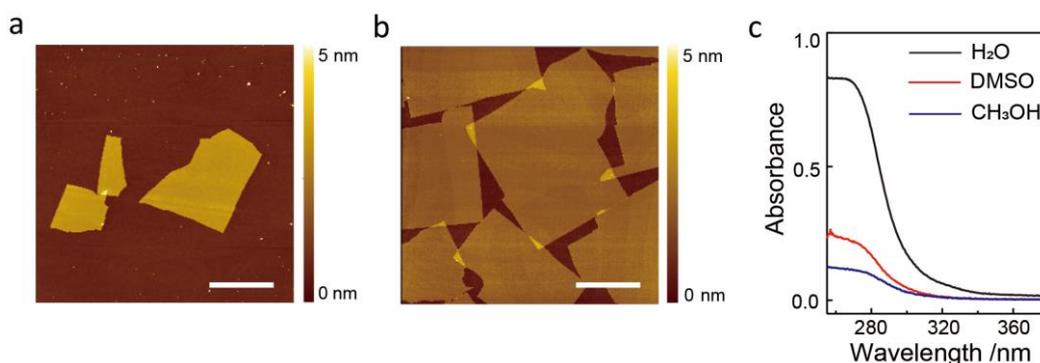


Figure 4. AFM images of the nanosheets produced via delamination in (a) CH₃OH and (b) DMSO. (c) A comparison of the UV-vis spectra of CH₃OH, DMSO, and H₂O suspensions. Scale bars are 5 μ m.

5. Conclusion

We systematically examined the osmotic swelling behaviors of layered perovskite niobate crystals, HCa₂Nb₃O₁₀·1.5H₂O, in aqueous solutions of organoammonium bases. Upon contact with the solutions, the layered crystals showed enormous expansion of the interlayer distance in the stacking direction up to 100-fold the original thickness. The extent of swelling of the layered crystals was not primarily dependent on the guest identity when the number of C atoms in the alkyl chains of the TAA ions varied from 1 to 4. In contrast, the strength of ion-ion interactions between the intercalants on the oxide layer was different depending on the size and hydrophobicity of the ions, which significantly affected the exfoliation behavior. The nanosheets exfoliated from swollen crystals with small ions (TMA and TEA) exhibited a large lateral size of ~8 μ m, but the exfoliation yield was under 10 %. Contrary to the former two ions, TPA and TBA effectively promoted exfoliation, but the nanosheet size was sub-micron as a result of severe fragmentation. In this work, we proved that the fragmentation of the nanosheets is ascribed neither to the application of a strong external shear force nor the mechanical stress imposed on the oxide layer upon the introduction of bulky ions but to hydrophobic interactions among the intercalants. Such interaction may induce the deformation of the oxide layers and finally break the nanosheets into small pieces. We found that this fragmentation can be suppressed by using organic

solvents instead of aqueous solution. Indeed, solvent replacement with organic solvent such as DMSO yielded well-shaped nanosheets with large dimensions even in the presence of TBA ions, supporting the idea that the chemical action among guest ions substantially influences the exfoliation mechanism.

This study broadens our understanding of the hydration-driven swelling of layered perovskite niobate crystals. We revealed that the exfoliation behavior due to swelling is closely associated with intermolecular interactions between TAA ions. Our approach to deepen the understanding of the exfoliation behavior of layered compounds represents a crucial step toward the tailored synthesis of 2D nanosheets.