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Formation of extraordinarily large nanosheets from $K_4Nb_6O_{17}$ crystals†

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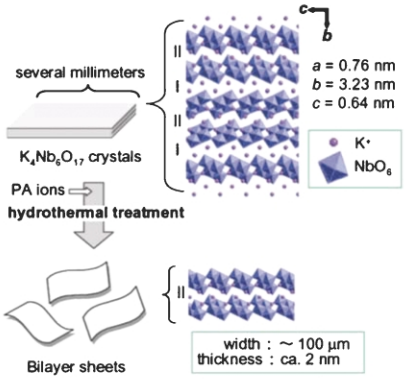
Exfoliated $K_4Nb_6O_{17}$ bilayer nanosheets in extraordinarily large size (*ca.* 100 μm) were prepared by the direct reaction of $K_4Nb_6O_{17}\cdot 3H_2O$ crystals with an aqueous solution of propylamine; the size was extremely larger than that of exfoliated nanosheets (several μm) reported previously.

Conversion of inorganic layered materials to nanosheets by exfoliation has attracted keen interest because nanosheets can be used as a component for novel supramolecular assemblies applicable in nanoscience and nanotechnology.[1] Exfoliation of layered crystals means the insertion of an infinite amount of solvent molecules into the interlayer region. Various materials composed of a wide variety of compositions and structures have been synthesized using exfoliated nanosheets. Suspensions or sols containing exfoliated nanosheets can be cast or spin-coated onto substrates to form thin films.[2] A layer by layer method has been utilized for the formation of more complex nanosystems using suspensions of inorganic layered materials.[3] Polymer–clay nanocomposites are a typical example of the use of exfoliated clay minerals.[4]

Exfoliation of layered materials, such as niobate,[5] titanate,[6] zirconium phosphate,[7] has often been studied from photo- and electrochemical viewpoints. The usual synthetic method to induce exfoliation includes ion exchange of interlayer alkali metal ions in these layered materials with protons and the following acid–base reactions of H-type materials with aqueous solutions of organoammonium ions.[8] However, the size of exfoliated nanosheets, reported so far, is limited to about several micrometers. It has been believed that only powder samples can be exfoliated. However, the present paper reports a successful use of single crystals for exfoliation.

$K_4Nb_6O_{17}$ (Scheme 1) is synthesized as single crystals by a flux method.[9] $K_4Nb_6O_{17}$ is quite interesting because it is transparent and semiconducting and the surface can orient dye species in one direction.[10] Here we report direct reaction of $K_4Nb_6O_{17}\cdot 3H_2O$ crystals with propylammoium (PA) ions under hydrothermal conditions without acid treatment. By using this method, we succeeded in preparing exfoliated nanosheets with ultra high aspect ratios if compared with the size of nanosheets reported hitherto. Although an increase in the viscosity of a suspension of niobate sols prepared by using propylammonium chloride has recently reported,[11] there have been no reports on the size of the nanosheets.



Scheme 1 Schematic image of exfoliation of $K_4Nb_6O_{17}$. $K_4Nb_6O_{17}$ possesses two interlayer environments (interlayer I and II) with different reactivities. Potassium ions in the interlayer I can be easily exchanged while those in the interlayer II are relatively difficult to replace.

n-Propylamine (1.0 ml) and water (20 ml) were added into thin plate-like transparent crystals of $K_4Nb_6O_{17}\cdot 3H_2O$ (0.10 g) with a size of several millimeters in width.‡ The mixture was sealed in a Teflon-lined vessel and allowed to stand at 120 °C. The mixture was not stirred to avoid the reduction of the size of exfoliated sheets during the reaction. After reaction for 1 d to 3 d, the slurry samples were swiftly and carefully analyzed by powder XRD. On the other hand, the slurry obtained after the reaction at 120 °C for 1 d was allowed to stand for a further day to separate a supernatant layer and precipitates. On separation, centrifugation was not used in order to avoid fragmentation.

The powder XRD patterns of the slurries varied with the reaction time (Fig. S1 ESI†). After 1 d, a broad peak at lower than 5° was observed as well as those due to $K_4Nb_6O_{17}\cdot 4.5H_2O$ (2.06 nm, 1.03 nm, and 0.69 nm) and the PA–$K_xNb_6O_{17}$ intercalation compound (2.21 nm, 1.12 nm, and 0.76 nm). When the reaction time was extended, the peaks due to both the hydrate and the intercalation compound disappeared and patterns characteristic of exfoliation[12] were observed in which the baseline increased with lowering of the diffraction angles. Consequently, the exfoliation was strongly suggested by intercalation of PA and the subsequent swelling with water to expand the interlayer space to the unlimited region.

The AFM image (Fig. S2 ESI†) of the sample in the supernatant clearly shows the presence of very thin nanosheets with a thickness of about 2 nm. The size of the plate direction is several micrometers and very similar to those reported previously using $K_4Nb_6O_{17}$ microcrystals.[13] Mallouk *et al.* estimated that $K_4Nb_6O_{17}$ nanosheets exfoliated with tetra-*n*-butylammonium (TBA) cations were bilayers.[13] Therefore, the nanosheets obtained here are bilayers where the interlayer I was exfoliated whereas the interlayer II was not affected.

On the other hand, the TEM image of the sample after the dispersion of the precipitates in water shows extraordinarily large nanosheets several tens of micrometers in width (Fig. 1). The sheet is almost transparent, indicating exfoliation to a higher degree. The thickness of the large nanosheets was estimated by AFM and the images are shown in Fig. 2. Nanosheets with a size from several tens of micrometers to 100 μm were clearly observed (Fig. 2a). On the basis of many AFM data, we can state that the distribution of the size mainly varied from 10 μm to *ca.* 100 μm. The thickness of the nanosheets was evaluated to be *ca.* 2 nm by using the image in which one nanosheet was placed on top of the other (Fig. 2b[14]). This means that the precipitates can also be exfoliated into nanosheets and that the size is much larger than that in supernatant.

When hexylamine (HA) was used instead of propylamine, exfoliation was not realized though an intercalation compound was formed. HA is relatively hydrophobic and can not entrain

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† Electronic supplementary information (ESI) available: powder XRD patterns of the slurries, AFM image of the sample in the supernatant, image of $K_4Nb_6O_{17}$ crystals. See http://www.rsc.org/suppdata/cc/b2/b206998a/

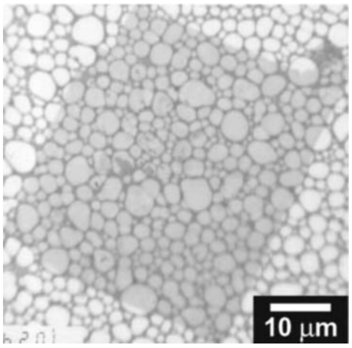

Fig. 1 TEM image of the sample after dispersing the precipitates (120 °C, 1 d) in water. The image was observed by a JEOL JEM-100CX microscope with an accelerating voltage of 100 kV.

water molecules after the intercalation. TBA cations were also directly reacted with large $K_4Nb_6O_{17}\cdot 3H_2O$ crystals. However, neither intercalation nor exfoliation was observed. Accordingly, the selection of PA is quite appropriate for this type of reaction.

Although the present results show that the large nanosheets are prepared, a substantial reduction in size was observed. Nanosheets with the size of 100 μm were obtained though large crystals of several millimeters were used. The AFM image (Fig. 2a) also shows the possible presence of some cracks. One of the reasons for this reduction in size is the influence of convection in an autoclave at 120 °C. The other one is possibly due to cleavage by hydration of the crystals during the reaction.

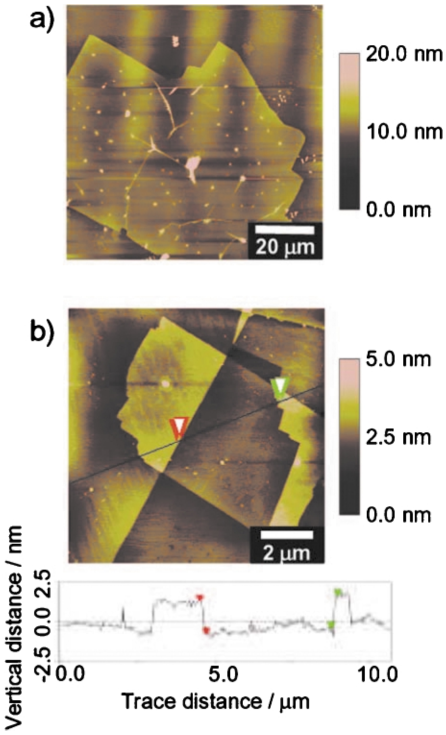

Fig. 2 AFM images of the sample on mica surfaces after dispersing the precipitates (120 °C, 1 d) in water. (a) 100 μm × 100 μm and (b) 10 μm × 10 μm. AFM images were recorded on a Nanoscope E (Digital Instruments) with contact mode (height mode).

In conclusion, we found the reaction conditions for the exfoliation of $K_4Nb_6O_{17}\cdot 3H_2O$ crystals by direct intercalation of PA. In the supernatant, nanosheets composed of bilayer sheets were formed with several micrometers in size. Nanosheets with 100 μm in size and about 2 nm in thickness were obtained from the precipitates and the size was much larger than those found previously. The research on various properties (electrical property, quantum size effect, and so on) of nanosheets themselves will be very interesting for nanotechnology. Films and nanocomposites using these large nanosheets will also be one of the next steps for applications.

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Notes and references

‡ Anhydrous $K_4Nb_6O_{17}$ crystals were synthesized according to a previous report.[9] K_2CO_3 (Wako Chemical Co., purity 99.99%) and Nb_2O_5 (Kanto Chemical Co., 99.95%) were mixed at the ratio of 2.7 : 3.0, and the mixture was heated at 1150 °C for 10 h to form anhydrous $K_4Nb_6O_{17}$. The crystals were hydrated to form $K_4Nb_6O_{17}\cdot 3H_2O$ thin plate-like crystals (see Fig. S3 ESI†). The powder XRD pattern of the crystals agreed well with that of $K_4Nb_6O_{17}\cdot 3H_2O$ of the JCPDS data file.[15]

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14 The dark area in the bottom may be due to bare surface of the substrate, the centre dark part is probably one nanosheet region, and the brightest region at the left-upper part should reflect overlaid nanosheets.
15 JCPDS data file 21-1297.