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Supporting information

Accordion-like swelling of layered perovskite crystals via massive permeation of aqueous solutions into 2D oxide galleries

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S-1. Preparation procedure of $KCa_2Nb_3O_{10}$ crystals

To obtain crystals of several tens of μm in size, the optimum starting mixture is a combination of K_2SO_4-$CaCO_3$-Nb_2O_5 with 5 : 4 : 3 in mol ratio, which corresponds to 20 mol% solute concentration (=solute/{solute+flux}). After ground in an agate mortar, the mixture was placed in a Pt crucible and heated in an electric furnace. At first, the mixture was heated to 900 ℃ at 300 ℃/h, and to 1300 ℃ at 100 ℃/h, and then kept at this temperature for 24 h. It was cooled down to 800 ℃ at a rate of 25 ℃/h and then the furnace was switched off. After removal of the flux in water and filtration of the product, $KCa_2Nb_3O_{10}$ crystals with the size in the range μm to several hundred μm were collected. No secondary phase was detected in the powder XRD profile as shown in Fig S-2(b).

S-2 Powder XRD patterns of $KCa_2Nb_3O_{10}$ before and after acid-exchange

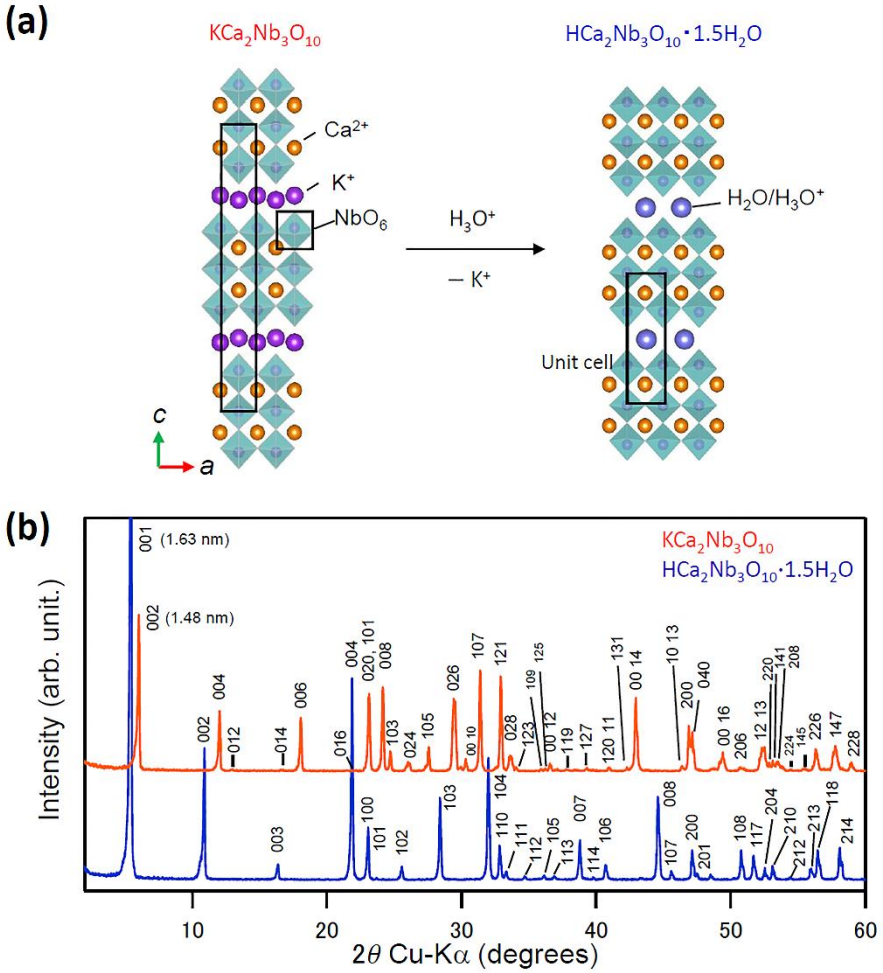

Fig. S-2 (a) Schematic structure of $KCa_2Nb_3O_{10}$ and that after the acid treatment ($HCa_2Nb_3O_{10}\cdot 1.5H_2O$). (b) XRD patterns of $KCa_2Nb_3O_{10}$ and $HCa_2Nb_3O_{10}\cdot 1.5H_2O$. All the observed peaks could be indexed on the basis of orthorhombic and tetragonal system, respectively.[1,2] The powder XRD was measured for $HCa_2Nb_3O_{10}\cdot 1.5H_2O$ at 80% RH. For $KCa_2Nb_3O_{10}$, the peaks were indexed with the order (*hlk*) instead of (*hkl*) for the convenience.[2]

S-3. SEM and composition analysis results before and after acid-exchange

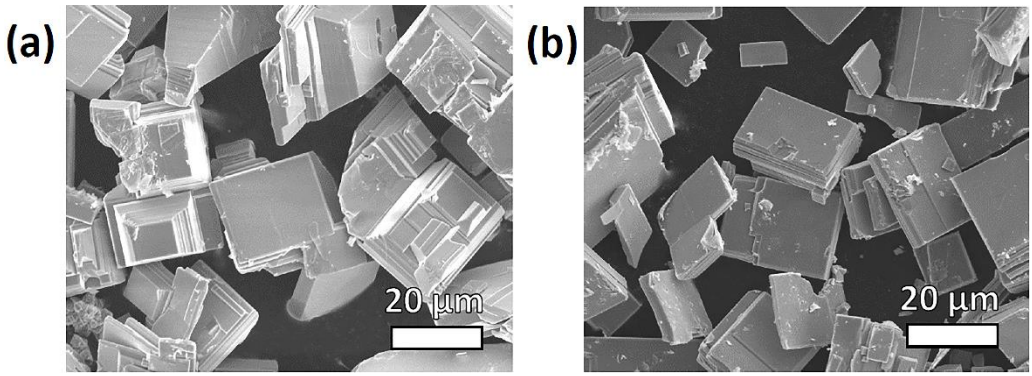

Fig. S-1 SEM images of (a) $KCa_2Nb_3O_{10}$ and (b) $HCa_2Nb_3O_{10}\cdot 1.5H_2O$ crystals. Outer crystal shape was maintained, while tiny cleaves appeared on the side facets of the crystals after the acid treatment.

Table. S-3 Compositions (wt%) of $KCa_2Nb_3O_{10}$ and $HCa_2Nb_3O_{10}\cdot 1.5H_2O$ crystals determined by chemical analysis.

Composition		K (%)	Ca (%)	Nb (%)	H_2O (%)
$KCa_2Nb_3O_{10}$	obsd.	7.14	13.9	49.3	-
	calcd.	7.01	14.4	50.0	-
$HCa_2Nb_3O_{10}\cdot 1.5H_2O$	obsd.	0.12	14.1	50.2	5.41
	calcd.	0.00	14.7	51.1	4.94

The exchange of K^+ in $KCa_2Nb_3O_{10}$ into H^+ was almost complete (98.3 %), and no dissolution of Ca and Nb was observed.

S-4. SEM images of the flux-grown $KCa_2Nb_3O_{10}$ crystals and polycrystals obtained by the solid-state calcination

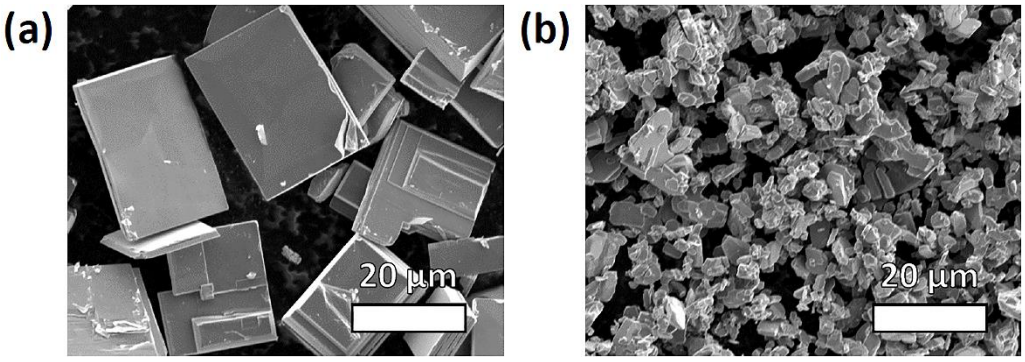

Fig. S-4 SEM images of (a) flux-grown $KCa_2Nb_3O_{10}$ crystals and (b) $KCa_2Nb_3O_{10}$ polycrystals synthesized by the conventional solid-state calcination method. Rectangular crystals with size several tens of μm were obtained in (a), while aggregates of tiny crystallites were observed in (b).

S-5. Model of TBA ion and its projected configuration on the perovskite layer

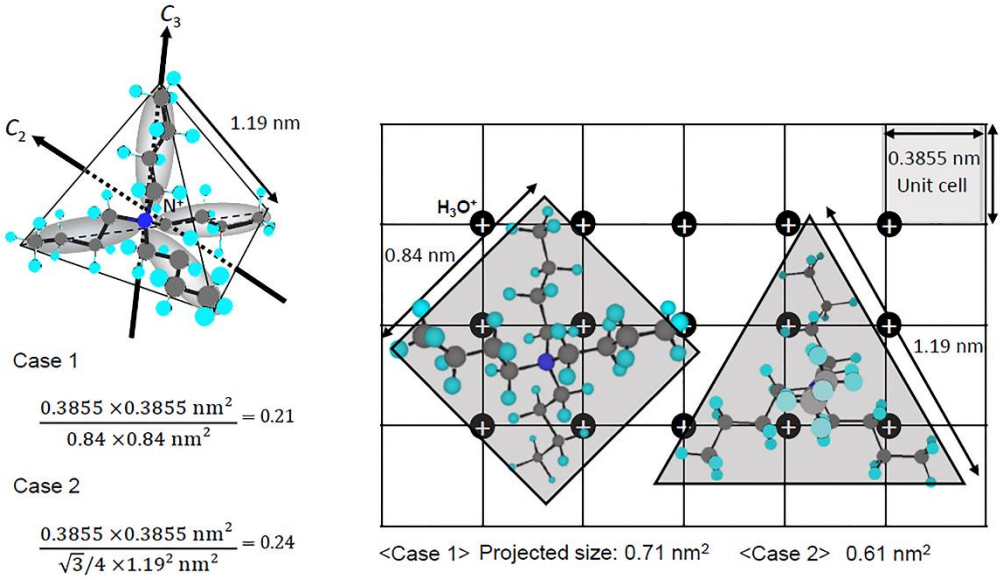

Fig. S-5 Schematic structure and projected sizes of TBA ion. The projected area can be varied from 0.61 to 0.71 nm^2 depending on its orientation.[3] The unit cell area is 0.149 nm^2, hence 0.21-0.24TBA ion covers a one side of the oxide layer. The layer has two faces, resultantly, 0.42-0.48TBA ion can be incorporated on a unit cell which is near to experimental value ~40 %. The molecular model was drawn using Chem 3D® (Cambridge Soft).

S-6. Comparison of swelling behaviors of the layered perovskite and layered titnate

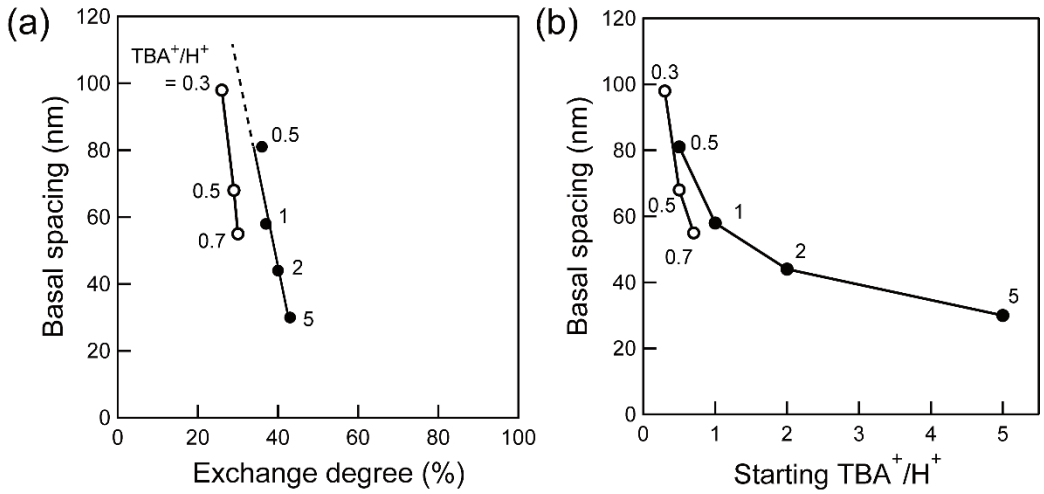

Fig. S-6 Expanded basal spacing as a function of (a) exchange degree expressed as percentage relative to the amount of H^+ in the crystal and (b) starting TBAOH concentration represented as the ratio of H^+ in the crystal. The filled symbol represents $HCa_2Nb_3O_{10}\cdot 1.5H_2O$ while the open symbol represents $H_{0.8}Ti_{1.2}Fe_{0.8}O_4\cdot H_2O$.[4] The maximum degree of swelling observed at the full exchange of TBA ions and then it decreased with increasing the TBA^+ concentration in the both systems.

S-7. Histograms of the swollen crystal length at various TBA^+ concentrations

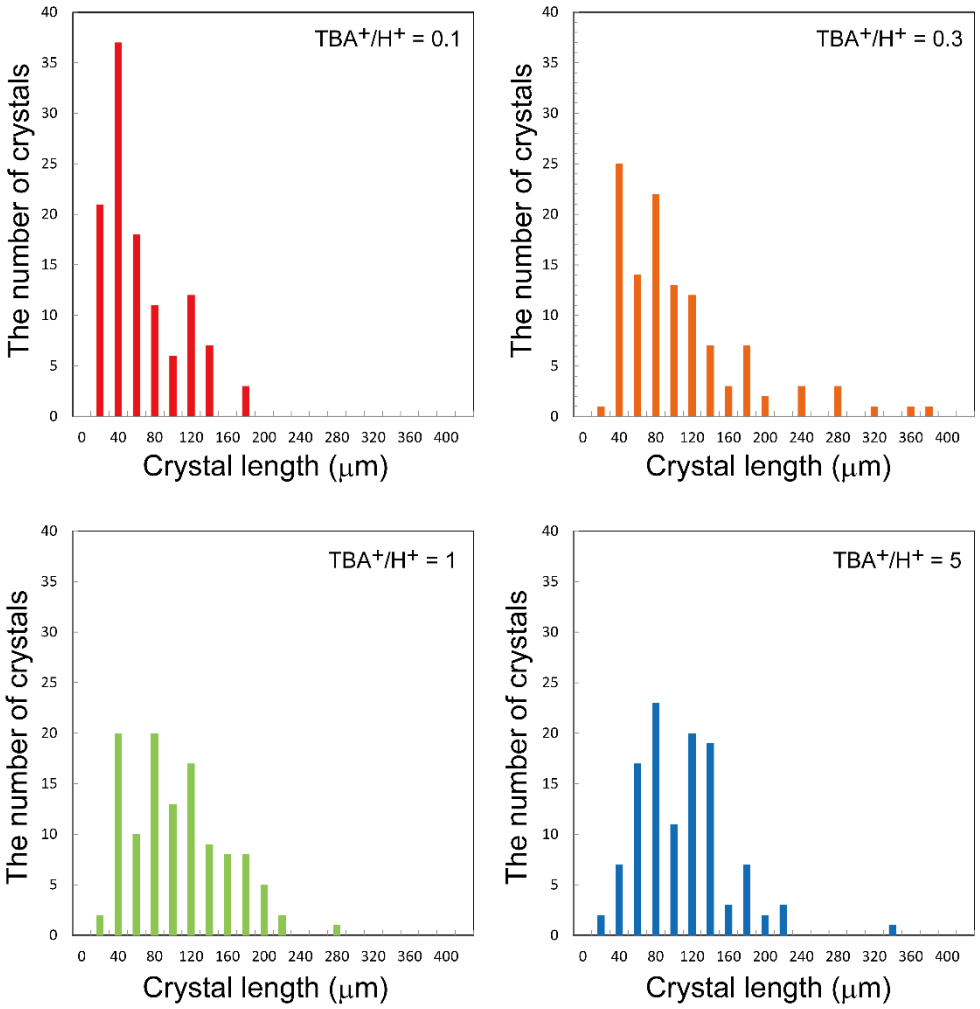

Fig. S-7 The length distribution of the swollen crystals with the TBAOH solutions at different concentrations (TBA^+/H^+ = 0.1-5). The histograms were made from the optical microscope images of each sample.

S-8 SEM images of the delaminated nanosheets

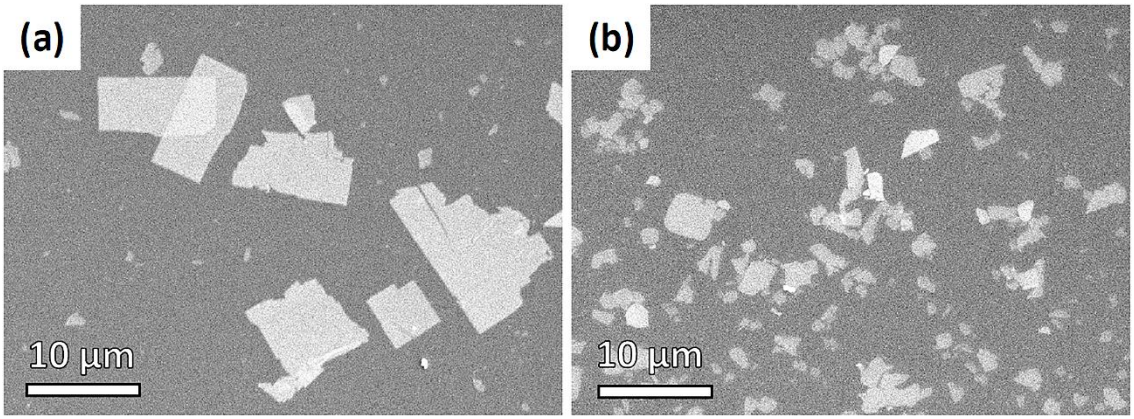

Fig. S-8 SEM images of $Ca_2Nb_3O_{10}^-$ nanosheets derived from (a) single crystal and (b) powder polycrystalline samples of $KCa_2Nb_3O_{10}$.

References

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