Preparation of Organic−Inorganic Hybrids Possessing Nanosheets with Perovskite-Related Structures via Exfoliation during a Sol−Gel Process

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Organic−inorganic hybrids containing exfoliated nanosheets with a perovskite-related structure have been prepared from an *n*-decoxy derivative of an ion-exchangeable layered perovskite, $HLaNb_2O_7 \cdot xH_2O$ (HLaNb) or $HCa_2Nb_3O_{10} \cdot xH_2O$ (HCaNb), silanol-terminated poly(dimethylsiloxane) (PDMS), and tetramethoxysilane (TMOS) via a sol−gel process involving the reaction of the *n*-decoxy derivative with a PDMS−TMOS mixture and subsequent intentional hydrolysis with hydrochloric acid. The X-ray diffraction (XRD) patterns of the resultant products after intentional hydrolysis indicate both preservation of the perovskite-like slab structure and disappearance of stacking order. Partial exfoliation of layered perovskites is correspondingly observed by transmission electron microscopy (TEM). The formation of a polysiloxane network composed of PDMS chains and Q^n units ($(RO)_{4-n}Si(OSi)_n$: R = H, CH_3) via intentional hydrolysis is shown by the solid-state ^{29}Si CP/MAS (cross-polarization and magic angle spinning) NMR spectroscopy. These products are expected to possess the Nb−O−Si linkage interface since a signal assignable to the $(SiO)Si(CH_3)_2O{-}Nb$ environment is present in the ^{29}Si CP/MAS NMR spectra of products prepared from an *n*-decoxy derivative of HLaNb (or HCaNb), PDMS, and TMOS in a similar manner without intentional hydrolysis and the Nb−O−Si bonds are expected to be preserved during hydrolysis. The exfoliated structures should be formed during the intentional hydrolysis process since the products prepared without intentional hydrolysis clearly exhibit a stacking order along the *c* axis.

Introduction

Organic−inorganic hybrids have been attracting significant attention as a new class of materials since the combination of an inorganic component and an organic component has the potential to provide improved and tunable properties.[1−5] Transition metal oxides are attractive inorganic components for hybrids since they exhibit a wide variety of properties.[4,6,7] Sol−gel processing is one of the promising routes to organic−inorganic hybrids since metal−oxygen networks can be formed using a "*Chimie Douce*" approach involving hydrolysis and polycondensation.[1−4,8−16] Thus, a large number of hybrids containing transition metal oxides have been prepared from transition metal alkoxides. It should be noted that crystalline transition metal oxides are generally favorable for enhancing the properties of hybrids.[4]

In addition to selection of an appropriate combination of inorganic and organic components, achieving desirable properties requires that their interfaces and nanostructures are carefully designed. Organic−inorganic hybrids can be classified into two groups, based on their interfaces:[1,2,4] class I hybrids with weak interactions and class II hybrids with strong bonds such as covalent bonds. For the production of class II hybrids,[1] selection of the preparation process and starting compounds is extremely important. In sol−gel processes, Si−C and Sn−C bonds are widely utilized as interfacial covalent bonds.[4] For hybrids containing transition metal oxides, on the contrary, M−O−Si bonds (M = transition metal) are frequently introduced at their interfaces[4] since covalent M−C and M−O−C bonds are unstable against hydrolysis.[17,18] One of the ideal nanostructures is a structure containing inorganic components with a well-defined domain size. The sol−gel process requires significant modification for the preparation of such structures since it

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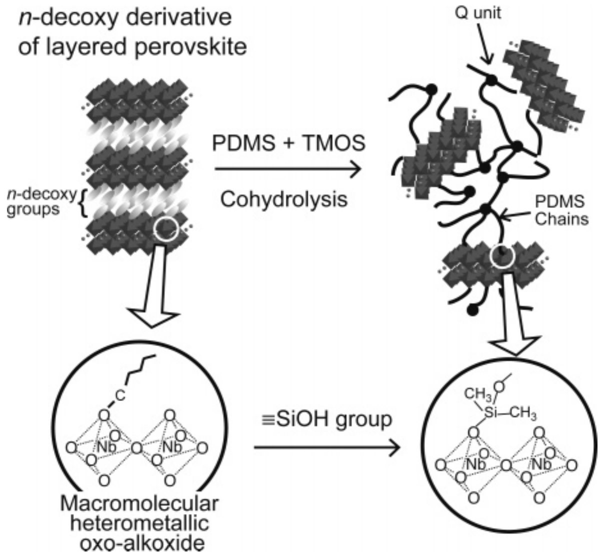
is generally very difficult to control the polycondensation process of metal alkoxides precisely. One of the proposed modifications is the use of well-defined oxo-clusters bearing alkoxy groups as inorganic nanobuilding blocks (NBBs),[4] but the relatively low stability of their core structures with respect to hydrolysis has limited their applicability to sol−gel processes. Instead, organic−inorganic hybrids have been prepared with NBBs bearing polymerizable groups, such as methacrylate groups, via copolymerization with organic monomers.[4,19,20]

The exfoliation of layered materials is another "*Chimie Douce*" technique for obtaining nanosheets with well-defined nanoscaled thicknesses, and if nanosheets possess reactive groups on their surfaces, they can be attractive candidates for inorganic NBBs for class II hybrids. As class I hybrids, layered material/polymer hybrids containing inorganic nanosheets have been extensively prepared through exfoliation.[5,21] Literature describing the preparation of class II layered material/polymer hybrids possessing interfacial covalent bonds, on the contrary, has been limited to date. A class II hybrid was prepared, for example, by polymerization of cyclo-siloxane in the interlayer space of a tetramethylammonium-$HTiNbO_5$ intercalation compound.[22] Another approach to preparation of class II hybrids was modification of the edges of the nanosheets of hectorite, with silanol-terminated polysiloxane[23] or with γ-methacryloxypropyl trimethoxysilanes or γ-methacryloxypropyl dimethyl ethoxysilanes, followed by polymerization.[24]

Here we report a novel sol−gel process for preparation of class II hybrids using crystalline nanosheets with perovskite-related structures as transition metal oxide NBBs. The *n*-alkoxy derivatives of ion-exchangeable layered perovskites, $HLaNb_2O_7{\cdot}xH_2O$ (HLaNb) and $HCa_2Nb_3O_{10}{\cdot}xH_2O$ (HCaNb), consisting of stacked perovskite-like slabs (the compositions originally present in the protonated forms are $[LaNb_2O_7]^-$ and $[Ca_2Nb_3O_{10}]^-$) bearing surface decoxy groups were utilized.[25−28] Cohydrolysis of an *n*-decoxy derivative of HLaNb (or HCaNb), silanol-terminated poly(dimethylsiloxane) [$HO(Si(CH_3)_2O)_nH$; PDMS], and tetramethoxysilane [$Si(OCH_3)_4$, TMOS] led to simultaneous occurrence of the formation of a condensed polysiloxane network (so-called organically modified silicates[15,16]) and exfoliation to form class II hybrids where nanosheets were dispersed in a condensed polysiloxane network with an Nb−O−Si linkage interface (Scheme 1).

Scheme 1. Overview of the Reaction of an *n*-Decoxy Derivative of an Ion-Exchangeable Layered Perovskite with a PDMS−TMOS Mixture and Subsequent Intentional Hydrolysis



Experimental Section

Preparation of the Organic−Inorganic Hybrids. Preparation of the intermediates, *n*-decoxy derivatives of HLaNb[27] and HCaNb,[28] was conducted based on previous reports. Typically, 0.1 g of the *n*-decoxy derivative was dispersed in a mixture of 3.0 mL of PDMS (molecular mass: ∼400−700) and 0.79 g of TMOS [($(CH_3)_2SiO$) unit (in PDMS):TMOS = 1:1 in a molar ratio], and the resulting suspension was stirred at 80 °C for 7 d. Hydrochloric acid (ca. 0.6 M) was then added dropwise to the suspension to achieve a nominal molar ratio of TMOS:H_2O:HCl = 1:4:0.045. After the mixture was stirred for 1 d under ambient atmosphere, the resultant product was dried under reduced pressure (*hydrolyzed* HLaNb−PDMS−TMOS or *hydrolyzed* HCaNb−PDMS−TMOS). For the investigation of the interfaces between the layered perovskites and polysiloxanes, 0.1 g of the *n*-decoxy derivative was dispersed in a mixture of 3.0 mL of PDMS and 0.79 g of TMOS at 80 °C for 7 d with no intentional hydrolysis procedure. The resultant product was then centrifuged, washed with tetrahydrofuran (THF), and dried at room temperature (HLaNb−PDMS−TMOS and HCaNb−PDMS−TMOS). In a similar fashion, typically 0.1 g of the *n*-decoxy derivative was dispersed in 5 mL of PDMS at 80 °C for 7 d. The resultant product was then centrifuged, washed with THF, and dried at room temperature (HLaNb−PDMS and HCaNb−PDMS).

For the investigation of the reaction process, 0.1 g of the *n*-decoxy derivative and 5 mL of trimethysilyl-terminated poly(dimethylsiloxane) {$(CH_3)_3SiO[Si(CH_3)_2O]_mSi(CH_3)_3$} (average molecular mass: ∼550) were stirred at 80 °C for 7 d. The resultant product was centrifuged, washed with THF, and dried at room temperature. In a similar fashion, 0.1 g of an *n*-decoxy derivative of a layered perovskite, HLaNb, was dispersed in 5 mL of TMOS at 80 °C for 7 d. The resultant product was then centrifuged, washed with THF, and dried at room temperature.

Instrumentation. The X-ray diffraction (XRD) patterns of the products were recorded with a Mac Science M03XHF[22] diffractometer with Mn-filtered Fe Kα radiation. The solid-state ^{13}C and ^{29}Si nuclear magnetic resonance (NMR) spectra were obtained using a JEOL CMX-400 spectrometer operated at 100.54 MHz (^{13}C) and 79.427 MHz (^{29}Si) using cross-polarization and magic angle spinning techniques (CP/MAS). The sample spinning rate was about 5 kHz. The contact time was 2 ms (^{13}C) or 5 ms (^{29}Si), and the

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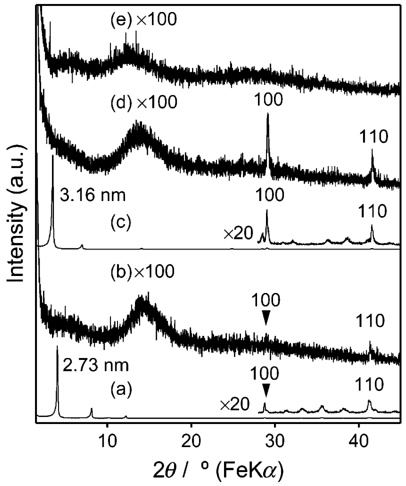

Figure 1. XRD patterns of (a) the *n*-decoxy derivative of HLaNb, (b) the reaction product of the *n*-decoxy derivative of HLaNb and PDMS-TMOS mixture with intentional hydrolysis (*hydrolyzed* HLaNb−PDMS−TMOS), (c) the *n*-decoxy derivative of HCaNb, (d) the reaction product of the *n*-decoxy derivative of HCaNb and PDMS−TMOS mixture with intentional hydrolysis (*hydrolyzed* HCaNb−PDMS−TMOS), and (e) the hydrolyzed PDMS−TMOS mixture.

pulse delay was 5 s. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-100CX microscope operated at 100 kV. Infrared (IR) adsorption spectra were recorded with a Perkin-Elmer Spectrum One instrument using the KBr disk technique.

Results and Discussion

Preparation of Organic−Inorganic Hybrids. Figure 1 demonstrates the XRD patterns of the *n*-decoxy derivatives of HLaNb and HCaNb as well as those of *hydrolyzed* HLaNb−PDMS−TMOS and *hydrolyzed* HCaNb−PDMS−TMOS. The interlayer distances of the *n*-decoxy derivatives are 2.73 nm (HLaNb) and 3.16 nm (HCaNb), consistent with the previous reports.[27,28] After cohydrolysis of the products obtained from the *n*-decoxy derivatives, PDMS and TMOS, the (00*l*) reflections of the *n*-decoxy derivatives disappear, while the (100) reflections at $2\theta = 28.9°$ (HLaNb) and 29.1° (HCaNb) and the (110) reflections at $2\theta = 41.4°$ (HLaNb) and 41.7° (HCaNb) are clearly present. Thus, although the long-range stacking order along the *c* axis disappears, the perovskite-like slab structures are preserved. A broad diffraction at around $2\theta = 13°$ can be ascribed to the condensed polysiloxane network based on a comparison with the XRD pattern of the hydrolyzed PDMS−TMOS mixture (Figure 1e).

The solid-state ^{29}Si CP/MAS NMR spectra of *hydrolyzed* HLaNb−PDMS−TMOS and *hydrolyzed* HCaNb−PDMS−TMOS are shown in Figure 2. Both the spectra show four signals at −19, −22, −100, and −109 ppm, and the signals at −22, −100, and −109 ppm are assignable to D^2 [$(CH_3)_2\mathit{Si}(OSi)_2$] (PDMS chain), Q^3 [$(RO)\mathit{Si}(OSi)_3$] [R = H, CH_3 (derived from TMOS)], and Q^4 [$\mathit{Si}(OSi)_4$] (derived from TMOS) environments, respectively.[29] The signal at −19 ppm can be ascribed to a *D*^{2}-Q [$(CH_3)_2\mathit{Si}(OSi)(OSi(O\text{-})_3)$] environment, indicating the successful formation of condensed polysiloxanes possessing a certain amount of bonds between the Q units and the PDMS chains via cohydrolysis.[16]

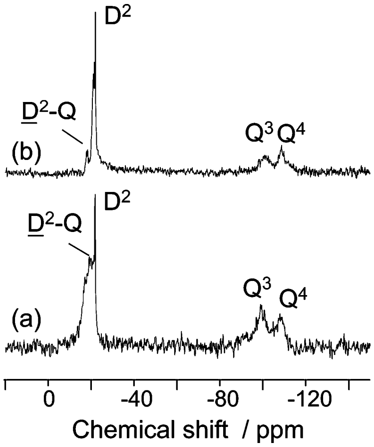

Figure 2. Solid-state ^{29}Si CP/MAS NMR spectra of (a) the reaction product of the *n*-decoxy derivative of HLaNb and the PDMS−TMOS mixture with intentional hydrolysis (*hydrolyzed* HLaNb−PDMS−TMOS) and (b) the reaction product of the *n*-decoxy derivative of HLaNb and the PDMS−TMOS mixture with intentional hydrolysis (*hydrolyzed* HCaNb−PDMS−TMOS).

Figures 3a and 3b show TEM images of *hydrolyzed* HLaNb−PDMS−TMOS and *hydrolyzed* HCaNb−PDMS−TMOS, respectively. Dark lines are clearly observed in the TEM images, and the thicknesses of the dark lines in both the images of *hydrolyzed* HLaNb−PDMS−TMOS (∼1 nm) and *hydrolyzed* HCaNb−PDMS−TMOS (∼1.5 nm) are closely consistent with the thickness of the individual perovskite-like slabs. Thus, it is clearly demonstrated that the perovskite-like slabs (dark lines) are dispersed in the polysiloxane network, a finding indicative of the formation of exfoliated hybrid structures. In addition to these structures, partially exfoliated particles consisting of stacked 3−5 perovskite-like slabs are also present; an example observed in *hydrolyzed* HCaNb−PDMS−TMOS is shown in Figure 3c.

Interfaces Formed between Perovskite-like Slabs and the Polysiloxane Network. To investigate the interfaces between perovskite-like slabs and the polysiloxane network, the reactions between the *n*-decoxy derivatives and PDMS are investigated. The XRD patterns of these products, HLaNb−PDMS and HCaNb−PDMS, are shown in Figure 4. After the reactions with PDMS, the new reflections appear at 1.41 nm (HLaNb−PDMS) and 1.85 nm (HCaNb−PDMS), which correspond to the interlayer distances. The presence of reflections at $2\theta = 28.8°$ (HLaNb−PDMS) and 29.1° (HCaNb−PDMS) indicates the preservation of the perovskite-like slab structures. These XRD results show that nanosheets (perovskite-like slabs) are stacked along the *c* axis in an ordered state.

Figure 5 shows the solid-state ^{13}C CP/MAS NMR of HLaNb−PDMS and HCaNb−PDMS. Both the spectra exhibit signals at 1 ppm, which are ascribable to methyl groups in the PDMS chain [$(\mathit{C}H_3)_2SiO$].[30] It is also notable with respect to both the spectra that the signals due to the

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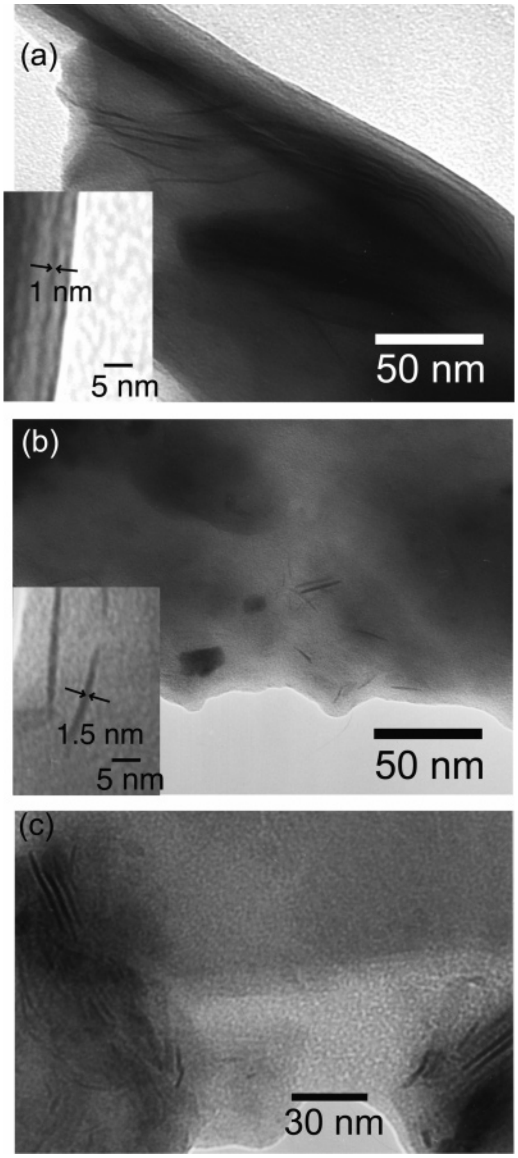

Figure 3. TEM images of (a) the reaction product of the *n*-decoxy derivative of HLaNb and the PDMS−TMOS mixture with intentional hydrolysis (*hydrolyzed* HLaNb−PDMS−TMOS), (b) the reaction product of the *n*-decoxy derivative of HCaNb and the PDMS−TMOS mixture with intentional hydrolysis (*hydrolyzed* HCaNb−PDMS−TMOS), and (c) partially exfoliated particles with layer stacking of 3−5 perovskite-like slabs of HLaNb. The inset images are magnifications of (a) and (b).

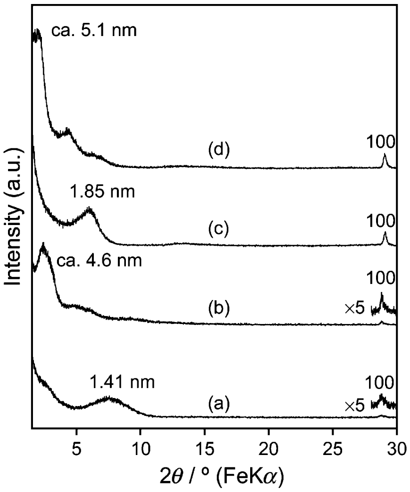

Figure 4. XRD patterns of (a) the reaction product of the *n*-decoxy derivative of HLaNb and PDMS (HLaNb−PDMS), (b) the reaction product of the *n*-decoxy derivative of HLaNb and the PDMS−TMOS mixture with no intentional hydrolysis (HLaNb−PDMS−TMOS), (c) the reaction product of the *n*-decoxy derivative of HCaNb and PDMS (HCaNb−PDMS), and (d) the reaction product of the *n*-decoxy derivative of HCaNb and the PDMS−TMOS mixture with no intentional hydrolysis (HCaNb−PDMS−TMOS).

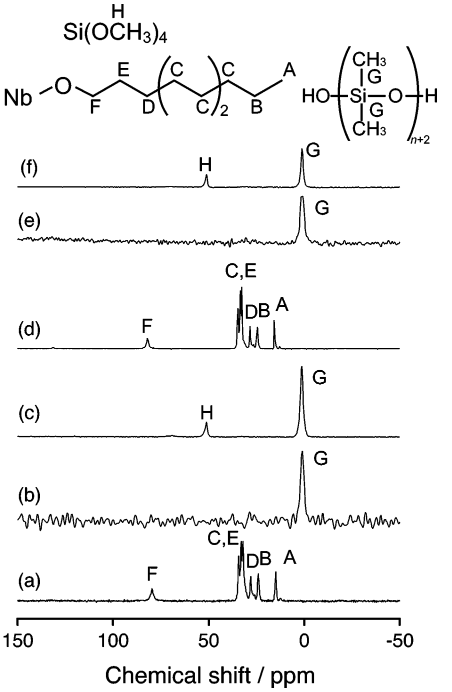

Figure 5. Solid-state ^{13}C CP/MAS NMR spectra of (a) the *n*-decoxy derivative of HLaNb, (b) the reaction product of the *n*-decoxy derivative of HLaNb and PDMS (HLaNb−PDMS), (c) the reaction product of the *n*-decoxy derivative of HLaNb and the PDMS−TMOS mixture with no intentional hydrolysis (HLaNb−PDMS−TMOS), (d) the *n*-decoxy derivative of HCaNb, (e) the reaction product of the *n*-decoxy derivative of HCaNb and PDMS (HCaNb−PDMS), and (f) the reaction product of the *n*-decoxy derivative of HCaNb and the PDMS−TMOS mixture with no intentional hydrolysis (HCaNb−PDMS−TMOS).

n-decoxy groups have disappeared, indicating that the *n*-decoxy groups on the interlayer surface are removed during the reaction. The IR spectra of HLaNb−PDMS and HCaNb−PDMS (not shown) revealed the presence of the bands at 1260, 1100−1000, and 800 cm^{-1}. These three bands can be ascribed to δ(Si−CH$_3$) (1260 cm^{-1}), ν(Si−O−Si) (1100−1000 cm^{-1}), and γ(Si−CH$_3$) (800 cm^{-1}) modes, a finding consistent with the presence of PDMS chains in the products.[31]

Solid-state ^{29}Si MAS NMR spectra of HLaNb−PDMS and HCaNb−PDMS are shown in Figure 6. Both the spectra show two signals at −5 and −22 ppm, the latter of which is ascribable to the D^2 environment of the PDMS chain [(CH$_3$)$_2$*Si*(OSi)$_2$].[29] The chemical shift of the broad signal (−5 ppm) is not consistent with the terminal D^1 environment of PDMS [(SiO)*Si*(CH$_3$)$_2$OH] (−11.0 ppm in a ^{29}Si NMR spectrum), and based on the reported chemical shift of an (SiO)*Si*(CH$_3$)$_2$O−Nb environment (−6.8 ppm),[30] it should be ascribed to the (SiO)*Si*(CH$_3$)$_2$O−Nb environment; the Nb−O−Si covalent bonds are formed between the interlayer surface of the layered perovskites and the end of PDMS chains.

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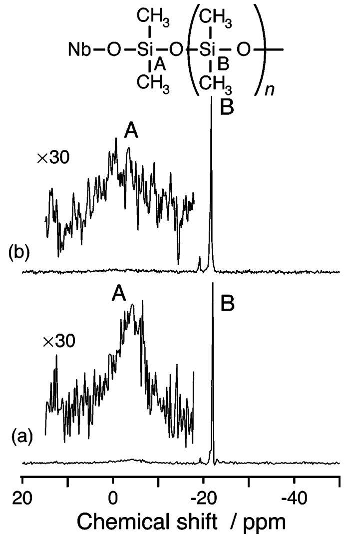

Figure 6. Solid-state ^{29}Si MAS NMR spectra of (a) the reaction product of the *n*-decoxy derivative of HLaNb with PDMS (HLaNb−PDMS) and (b) the reaction product of the *n*-decoxy derivative of HCaNb with PDMS (HCaNb−PDMS).

We further investigated the interface of organic−inorganic hybrids prepared from the *n*-decoxy derivatives, PDMS and TMOS without intentional hydrolysis, HLaNb−PDMS−TMOS and HCaNb−PDMS−TMOS. When crude reaction products from the *n*-decoxy derivative and the PDMS−TMOS mixture were washed with THF without the addition of any water, the XRD patterns of the resulting products showed new reflections at ca. 4.6 nm (HLaNb) and ca. 5.1 nm (HCaNb), as shown in Figure 4. These interlayer distances could not be determined precisely since the broad reflections are expected to be composed of overlapping reflections with different interlayer distances, as indicated by a shoulder appearing at 2.8° in HLaNb−PDMS−TMOS. The presence of the (100) reflections at 28.8° (HLaNb−PDMS−TMOS) and 29.1° (HCaNb−PDMS−TMOS) indicates the preservation of perovskite-like slab structures. These results exhibit the presence of a stacking order along the *c* axis before intentional hydrolysis.

Solid-state ^{13}C CP/MAS NMR spectra of HLaNb−PDMS−TMOS and HCaNb−PDMS−TMOS are shown in Figure 5. No signals due to *n*-decoxy groups are observed, a result similar to the reactions with PDMS. Instead, the signals of methyl groups in the PDMS chains, a [$(CH_3)_2SiO$] environment (1 ppm),[30] and methoxy groups originating from TMOS, an [$\equiv Si(OCH_3)$] environment (51 ppm), are detected. These results indicate that the *n*-decoxy groups on the interlayer surface are completely removed before the intentional hydrolysis.

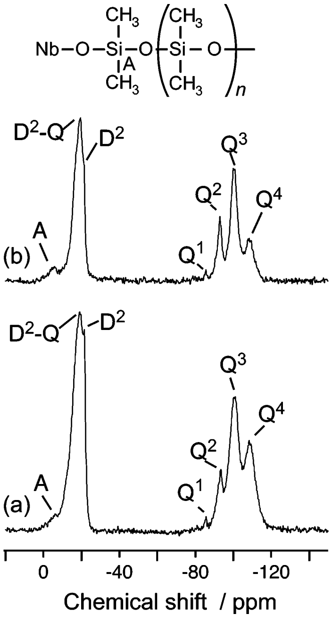

Figure 7. Solid-state ^{29}Si CP/MAS NMR spectra of (a) the reaction product of the *n*-decoxy derivative of HLaNb and the PDMS−TMOS mixture with no intentional hydrolysis (HLaNb−PDMS−TMOS) and (b) the reaction product of the *n*-decoxy derivative of HCaNb and the PDMS−TMOS mixture with no intentional hydrolysis (HCaNb−PDMS−TMOS).

Solid-state ^{29}Si CP/MAS NMR spectra of HLaNb−PDMS−TMOS and HCaNb−PDMS−TMOS are shown in Figure 7. Both the spectra exhibit D^2-Q (−19 ppm), D^2 (−22 ppm), Q^1 [$(RO)_3Si(OSi)$] (R = H, CH_3) (−85 ppm), Q^2 [$(RO)_2Si(OSi)_2$] (−93 ppm), Q^3 (−101 ppm), and Q^4 (−108 ppm) environments, indicating the formation of a polysiloxane network via hydrolysis−condensation, probably initiated by water present as an impurity and/or produced by condensation of a part of PDMS.[16,29] Signals due to the Q^1 and Q^2 environments are observed in the products without intentional hydrolysis, while the polysiloxane network of the hydrolyzed products, *hydrolyzed* HLaNb−PDMS−TMOS and *hydrolyzed* HCaNb−PDMS−TMOS, consists of Q^3 and Q^4 environments only, indicating that the Q units are in a highly condensed state after intentional hydrolysis. In addition, broad shoulders are detected at around −5 ppm, presenting clear evidence for the presence of the (SiO)-$Si(CH_3)_2O$−Nb environment in the hybrids.[30] The products without intentional hydrolysis, HLaNb−PDMS−TMOS and HCaNb−PDMS−TMOS, can therefore be classified as graft-type class II hybrids.

Mechanism of the Reaction between Layered Perovskites and the PDMS-TMOS Mixture. We first discuss the reaction of the *n*-decoxy derivative of HLaNb (or HCaNb) with PDMS. The Nb−O−Si bonds are formed by the reaction between ≡SiOH groups of PDMS and the surface of perovskite-like slabs, as shown in the ^{29}Si CP/MAS NMR spectra of the products, HLaNb−PDMS and HCaNb−PDMS. When we attempted a reaction between an *n*-decoxy derivative of HLaNb and trimethylsilyl-terminated poly(dimethylsiloxane), $\{(CH_3)_3SiO[Si(CH_3)_2O]_mSi(CH_3)_3\}$, the XRD pattern of the product showed reflections due to an *n*-decoxy derivative of HLaNb only, indicating that no intercalation nor exfoliation occurs; the ≡SiOH groups are required for the reaction between an *n*-decoxy derivative and PDMS.

Reactions between *n*-decoxy derivatives and PDMS are, therefore, expected to be similar to those between *n*-alkoxy derivatives and alcohols, the so-called alcohol-exchange-type reactions,[25,27,28] that require the presence of water in the system. Since water must be present as an impurity and/or produced by condensation between the ≡SiOH groups of PDMS in the present system, the reaction is expected to proceed in two steps: a part of the (n-$C_{10}H_{21}O$)NbO_5 group is hydrolyzed to form an (HO)NbO_5 site, and the subsequent reaction between the (HO)NbO_5 site and PDMS leads to the formation of $\{-O[Si(CH_3)_2O]_{n-1}\}-Si(CH_3)_2O-NbO_5$ groups. The reaction between an *n*-decoxy derivative and PDMS can therefore be expressed as follows:

$$(n\text{-}C_{10}H_{21}O)NbO_5 + H_2O \rightarrow (HO)NbO_5 + n\text{-}C_{10}H_{21}OH \quad (1)$$

$$\{-O[Si(CH_3)_2O]_{n-1}\}-Si(CH_3)_2OH + (HO)NbO_5 \rightarrow \{-O[Si(CH_3)_2O]_{n-1}\}-Si(CH_3)_2O-NbO_5 + H_2O \quad (2)$$

The products of the reaction between an *n*-decoxy derivative of HLaNb (or HCaNb) and PDMS−TMOS mixture without intentional hydrolysis, HLaNb−PDMS−TMOS and HCaNb−PDMS−TMOS, also possess Nb−O−Si bonds, as shown in their ^{29}Si CP/MAS NMR spectra, indicating that the reaction mechanism is very similar to that between an *n*-alkoxy derivative of HLaNb (or HCaNb) and PDMS. Since the Nb−O−Si bonds are stable against hydrolysis,[4] the Nb−O−Si bonds, once formed in the products of a reaction between an *n*-decoxy derivative of HLaNb (or HCaNb) and PDMS−TMOS mixture before intentional hydrolysis (see previous section "Interfaces Formed between Perovskite-like Slabs and the Polysiloxane Network"), should be preserved in the exfoliated hybrids prepared via intentional hydrolysis, *hydrolyzed* HLaNb−PDMS−TMOS and *hydrolyzed* HCaNb−PDMS−TMOS. The exfoliated hybrids, *hydrolyzed* HLaNb−PDMS−TMOS and *hydrolyzed* HCaNb−PDMS−TMOS, should consequently also be classified as class II hybrids.

Based on a report on a reaction between PDMS and tetraethoxysilane (TEOS),[15] cohydrolysis between PDMS and TEOS leads to the formation of a silica-like region, which provides cross-linking points. Since the solid-state ^{29}Si CP/MAS NMR spectra of *hydrolyzed* HLaNb−PDMS−TMOS and *hydrolyzed* HCaNb−PDMS−TMOS are very similar to those of cohydrolysis products from PDMS−TEOS mixtures (not shown), silica-like regions providing a cross-linking point are also expected to be present in *hydrolyzed* HLaNb−PDMS−TMOS and *hydrolyzed* HCaNb−PDMS−TMOS.

The interactions of Q^n environments with the *n*-decoxy derivatives are also investigated through the reaction between *n*-decoxy derivative of HLaNb and TMOS without intentional hydrolysis. An XRD pattern of the product of a reaction between the *n*-decoxy derivative of HLaNb and TMOS without intentional hydrolysis showed a decrease in the interlayer distance from 2.73 to 1.46 nm. Solid-state ^{13}C CP/MAS NMR spectroscopy showed the presence of no *n*-decoxy groups. The solid-state ^{29}Si CP/MAS NMR spectrum of the product showed signals due to the Q^1 and Q^2 environment, indicating the formation of oligomeric and/or polymeric polysiloxane through hydrolysis−condensation of TMOS by impurity water. These results indicate that TMOS molecules and/or silicate polymer derived from TMOS can be intercalated into the interlayer space of HLaNb. We cannot find spectroscopic evidence, however, for the presence of Nb−O−Si bonds formed by the reaction involving *n*-decoxy derivative of HLaNb and TMOS only, mainly because no clear shift of ^{29}Si NMR signals has been reported upon the formation of M−O−Si bonds.

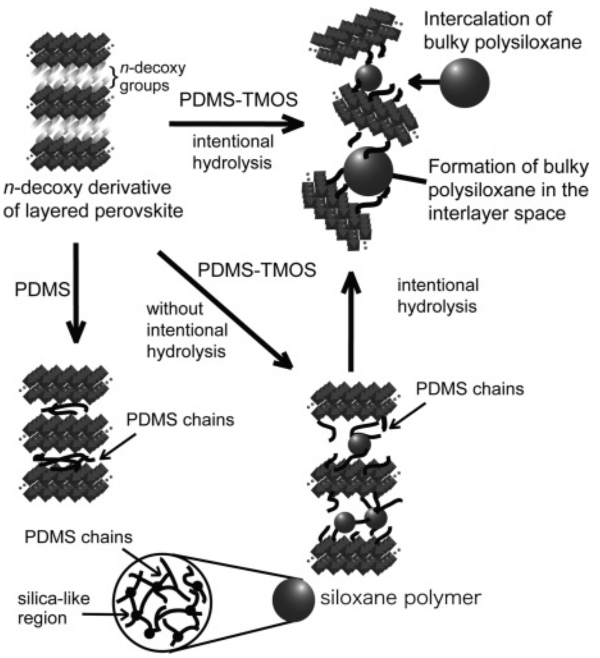

Figure 8. Proposed model for exfoliation behavior.

Exfoliation Behavior of Layered Perovskites. The XRD patterns and TEM images of hydrolyzed products, *hydrolyzed* HLaNb−PDMS−TMOS and *hydrolyzed* HCaNb−PDMS−TMOS, show that the stacking order disappears along the *c* axis (a characteristic typically observed with exfoliated hybrids[32]), while the products without intentional hydrolysis, HLaNb−PDMS−TMOS and HCaNb−PDMS−TMOS, possess a stacking order along the *c* axis (graft-type hybrids). Since intentional hydrolysis leads to the formation of a condensed polysiloxane network, the intercalation of condensed polysiloxane and/or development of a polysiloxane network in the interlayer space are expected to occur during intentional hydrolysis to induce exfoliation of the layered perovskite. Figure 8 demonstrates the proposed model for the exfoliation process.

When we attempted a reaction of HLaNb, or of an *n*-propoxy derivative of HLaNb possessing a smaller interlayer distance than that of the *n*-decoxy derivative of HLaNb, with PDMS, the XRD patterns of the reaction products showed a reflection due to unreacted HLaNb at 10.6° (1.05 nm) or *n*-propoxy derivative of HLaNb at 7.21° (1.54 nm) only, indicating no intercalation of PDMS in the interlayer space of HLaNb or the *n*-propoxy derivative of HLaNb. We also attempted a reaction of HLaNb or the *n*-propoxy derivative of HLaNb with the PDMS−TMOS mixture with subsequent intentional hydrolysis. The XRD pattern of the reaction product from HLaNb showed a reflection of HLaNb only at 10.6° (1.05 nm), indicating that the reaction did not occur. When the *n*-propoxy derivative of HLaNb was used as an intermediate, the XRD pattern showed a reflection at 10.2° (1.09 nm). Based on the interlayer distance of HLaNb (1.05 nm), this reflection at 10.2° seems to be assignable to HLaNb, suggesting that the *n*-propoxy groups on the interlayer surface are hydrolyzed to form HLaNb; the reaction between the *n*-propoxy derivative of HLaNb and

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(32) Giannelis, E. P. *Adv. Mater.* **1996**, *8*, 29.

the PDMS−TMOS mixture also failed to occur. The use of an intermediate with a larger interlayer distance is consequently important for exfoliation of layered perovskites.

Conclusions

We have demonstrated a new sol−gel approach involving exfoliation of the *n*-decoxy derivatives of ion-exchangeable layered perovskites to prepare class II hybrids. Cohydrolysis of the *n*-decoxy derivative of an ion-exchangeable layered perovskite (HLaNb or HCaNb), PDMS, and TMOS by hydrochloric acid leads to the formation of organic−inorganic hybrids possessing exfoliated perovskite-like slabs, nanosheets with perovskite-related structures. Nb−O−Si covalent bonds, which bind PDMS chains to the exfoliated perovskite-like slabs, are formed during the reaction of an *n*-decoxy derivative of an ion-exchangeable layered perovskite with PDMS or a PDMS−TMOS mixture with no intentional hydrolysis process. Since the Nb−O−Si bonds are expected to be stable with respect to hydrolysis, the reaction products of the *n*-decoxy derivatives of ion-exchangeable layered perovskites with a PDMS−TMOS mixture with an intentional hydrolysis process should also be class II hybrids with an Nb−O−Si linkage interface. Since the product obtained with no intentional hydrolysis possesses the stacking order of perovskite-like slabs along the *c* axis, the hydrolysis process must induce the exfoliation of layered perovskites. Although class-I-type layered material/polymer hybrids created through exfoliation have been extensively studied, the present approach appears to be applicable to a variety of class II hybrids whose properties can be tuned by selecting appropriate nanosheets, as NBBs.

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