Preparation of a nanocomposite consisting of a siloxane network and perovskite-related nanosheets via a sol–gel process

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Abstract

A nanocomposite possessing perovskite-related nanosheets dispersed in a siloxane network was prepared by cohydrolysis of the n-decoxy derivative of an ion-exchangeable layered perovskite, HCa₂Nb₃O₁₀·xH₂O (HCaNb), and tetramethoxysilane (TMOS) via a sol–gel process involving exfoliation. In the X-ray diffraction (XRD) pattern of the product after drying for 1 d, the (0 0 l) reflections disappeared. The transmission electron microscopy (TEM) image of the product after drying for 1 d showed dark lines with a thickness of 1.5 nm, which was consistent with the thickness of an individual nanosheet, indicating exfoliation of HCaNb. In the XRD patterns of the reaction products of the n-decoxy derivative of HCaNb and TMOS before drying and after drying for 60 min, (0 0 l) reflections were detected. After drying for 80 min, the intensity of the (0 0 l) reflections decreased. The intensity decreased with an increase in the drying time, indicating that the exfoliation of HCaNb occurred during the drying process.

1. Introduction

The dispersion of inorganic crystals in inorganic amorphous matrices has been conducted to prepare photocatalysts, non-linear optical materials and ferroelectric materials [1–4]. The sol–gel process is one of the common approaches to preparation of these types of materials, since the sol–gel process leads to the facile formation of metal-oxygen networks [5]. If metal alkoxides are the only source of metals, however, it is generally difficult to prepare nanocomposites possessing inorganic crystals via the sol–gel process; heat treatment is required to crystallize desirable crystals from amorphous metal-oxygen networks formed through the sol–gel process. It should also be noted that control of the crystal size in nanocomposites is difficult through the sol–gel process and subsequent heat treatment [6]. One approach to overcome this drawback is the use of clusters (nanobuilding blocks) with well-defined sizes and crystal structures [7]. The lower stability of the core structures of nanobuilding blocks against hydrolysis limits application of the approach, however, to systems involving polymerization between organic functional groups bound on the surface of nanobuilding blocks [8]: it is very difficult to disperse nanobuilding blocks in inorganic matrices.

Layered materials consist of regularly stacked nanosheets, and some of the layered materials exhibit exfoliation behavior through intercalation to form isolated nanosheets, which can be regarded as nanobuilding blocks. Nanocomposites possessing nanosheets in polymer matrices via exfoliation of layered materials have therefore been extensively investigated [9,10]. Since the sol–gel process generally leads to the formation of metal-oxygen networks, which can be regarded as inorganic polymers, through hydrolysis and condensation, combination of intercalation and the sol–gel process can be employed to prepare nanocomposites possessing nanosheets in inorganic matrices. A typical example is a silica-clay nanocomposite that was prepared by hydrolysis and condensation of tetramethoxysilane (TMOS) in the presence of a cetyltrimethylammonium-montmorillonite...
intercalation compound [11]. It is known that the interface between the nanosheets (nanobuilding blocks) and the polymer matrix considerably affect the properties of the nanocomposites [7]. In the silica-clay nanocomposite, since montmorillonite possesses no reactive groups on its interlayer surface, there should be no strong chemical bond, such as a covalent bond, between the nanosheet surface and the siloxane network.

We recently reported the preparation of organic–inorganic hybrids by a combination of a grafting reaction on the nanosheet surface and the sol–gel process [8]. Cohydration of the n-alkoxy derivative of an ion-exchangeable layered perovskite, HLaNb2O7·xH2O or HCa2Nb3O10·yH2O [13–16], TMOS, and a silanol-terminated polydimethylsiloxane (PDMS) led to the formation of hybrids possessing exfoliated nanosheets with a perovskite-related structure in organopolysiloxane networks [12]. The Nb–O–Si linkages between the surfaces of the perovskite-related nanosheets and the organopolysiloxane networks were formed through these reactions. It is worth noting that nanosheets with a perovskite-related structure can be considered to be nanobuilding blocks with high reactivity, stability with respect to hydrolysis and an anisotropic structure.

We report here the preparation of an inorganic–inorganic nanocomposite possessing nanosheets with a perovskite-related structure in a siloxane network by cohydration of TMOS and an n-decoxy derivative of a protonated form of an ion-exchangeable layered perovskite, HCa2Nb3O10·xH2O. In particular, we focused on the exfoliation behavior upon drying.

2. Experimental

2.1. Synthesis of the layered perovskite-siloxane nanocomposite

The n-decoxy derivative of HCaNb was prepared based on an earlier report [15]. For cohydration of the n-decoxy derivative of HCaNb and TMOS, 0.1 g of the n-decoxy derivative of HCaNb and 1.2 mL of TMOS were stirred in 3 mL of acetonitrile (n-decoxy derivative of HCaNb: TMOS ≈ 1:50 (C10H21O-Nb site: CH3O-group in TMOS ≈ 1:200) in a molar ratio, TMOS:CH2CN = 1:2.5 in a volume ratio). A mixture of 3 mL of acetonitrile and 0.59 mL of hydrochloric acid (1.1 × 10⁻⁴ mol/L) was added dropwise to the suspension to achieve a molar ratio of TMOS:H2O:HCl = 1:4.8 × 10⁻⁵. (Acetonitrile was added to achieve a volume ratio of 1:2.5. In the overall system, the volume ratio of TMOS:CH2CN was 1:5.) After stirring at 60 °C for 1 d, a gel formed, and this was dried further at 80 °C for 1 d (TMOS-HCaNb). For investigation of the exfoliation behavior, the gel formed by the reaction of the n-decoxy derivative of HCaNb and TMOS was also dried at 80 °C for 60 and 80 min. To obtain a TEM image of the gel without drying, the gel was dried using a freeze-drying technique.

For investigation of the reaction mechanism, 2.88 mL of n-butanol and 0.1 g of n-decoxy-HCaNb and 0.59 mL of hydrochloric acid (1.1 × 10⁻³ M) were stirred in 14.4 mL of acetonitrile for 7 d (molar ratio of the n-decoxy derivative of HCaNb:BuOH ≈ 1:200). A mixture of 0.1 g of the n-octylamine-HCaNb intercalation compound, prepared based on an earlier report [17], and TMOS was hydrolyzed in a similar fashion (molar ratio of n-octylamine-HCaNb intercalation compound: TMOS ≈ 1:50, TMOS:H2O:HCl = 1:4.8 × 10⁻⁵).

2.2. Instrumentation

The X-ray diffraction (XRD) patterns of the products were obtained using a Rigaku RINT-1100 diffractometer with Mn-filtered FeKα radiation. The solid-state ¹³C and ²⁹Si nuclear magnetic resonance spectra were recorded using a JEOL CMX-400 spectrometer operated at 100.54 MHz (¹³C) and 79.427 MHz (²⁹Si). The solid-state ¹³C NMR was operated with cross polarization and magic angle spinning techniques (CP/MAS) at a spinning rate of about 5 kHz. The contact time was 1.5 ms, and the pulse delay was 5 s. The solid-state ²⁹Si NMR was operated with MAS technique at a spinning rate of about 5 kHz. The pulse delay was 200 s. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-100CX microscope operated at 100 kV.

3. Results and discussion

3.1. Synthesis of the layered perovskite-siloxane nanocomposite

Fig. 1 shows the XRD patterns of the n-decoxy derivative of HCaNb and TMOS-HCaNb. In the XRD pattern of the n-decoxy derivative of HCaNb, a (0 0 1) reflection due to an interlayer distance is detected at 2θ = 3.37°, d001 = 3.29 nm, with higher orders, a result consistent with the previously reported interlayer distance of the n-decoxy derivative of HCaNb [15]. After cohydration with TMOS and subsequent drying at 80 °C for 1 d, the (0 0 1) reflections disappear. The (1 0 0) and (1 1 0) reflections resulting from a perovskite-like slab structure, on the contrary, are observed at 2θ = 29.2° and 41.7°, respectively; these reflections do not shift upon cohydration. These results indicate the disappearance of the stacking order along the c-axis and preservation of the perovskite-like slab structure of the nanosheets.

TEM images of TMOS-HCaNb are shown in Fig. 2(a) and (b). Dark lines are observed with a thickness of ca. 1.5 nm (Fig. 2(a)), which is in excellent consistency with the thickness of the perovskite-like slabs of [Ca2Nb3O10]n−, suggesting that the dark lines correspond to an individual perovskite-related nanosheets. These results suggest the occurrence of exfoliation of layered perovskites. The presence of two stacked perovskite-related nanosheets
hydrolysis of TMOS in the presence of a cetyltrimethylammonium-montmorillonite intercalation compound led to the exfoliation of montmorillonite [11], while no exfoliation of HCaNb occurred with hydrolysis of TMOS in the presence of the n-octylamine-HCaNb intercalation compound. The difference could be attributed to different swelling behavior: when the n-octylamine-HCaNb intercalation compound was dispersed in acetonitrile, no swelling behavior was observed, while montmorillonite in water exhibited swelling behavior. We examined the effect of solvent on the alcohol-exchange-type reaction. When we conducted a reaction of the n-deoxy derivative of HCaNb and n-butanol in acetonitrile at 60 °C, the XRD pattern of the product (not shown) showed the (0 0 1) reflection at 2θ = 4.18° but no reflection due to the n-deoxy derivative of HCaNb. In the solid-state 13C CP/MAS NMR spectrum of the product (not shown), signals due to n-butoxy groups were observed at 14, 29, 35 and 82 ppm, and the signals due to n-deoxy groups disappeared. These results suggest the successful occurrence of an alcohol-exchange-type reaction in acetonitrile at 60 °C. It is therefore reasonable to assume that the n-deoxy derivative of HCaNb can also behave as a kind of a giant heterometallic alkoxide in acetonitrile. These results indicate that the alkoxy groups on the surface in the n-deoxy derivative of HCaNb play a key role in the reaction process. Based on an earlier report that the reaction of the n-deoxy derivative of HCaNb and PDMS led to the formation of the Nb–O–Si bond by an alcohol-exchange-type reaction with SiOH groups [12], the Nb–O–Si bond might be formed during the reaction of the n-deoxy derivative of HCaNb and the SiOH groups. We cannot find any spectroscopic evidence, however, for the formation of Nb–O–Si bonds by 29Si NMR and XPS.

3.2. Exfoliation process

We investigated exfoliation behavior upon drying. The reaction products of the n-deoxy derivative of HCaNb and TMOS before drying were dried for 60 and 80 min. Although the gel after drying 1 d was xerogel, the gels after drying for 60 and 80 min were in a wet-gel state. Figs. 1(c)–(e) show the XRD patterns of the reaction products of the n-deoxy derivative of HCaNb and TMOS before drying and after drying for 60 and 80 min. In the XRD pattern of the product before drying, the (0 0 1) reflection due to the interlayer distance is observed at 2θ = 3.36° (d001 = 3.30 nm). The (0 0 1) reflection is still clearly detected in the XRD pattern of the gel after drying for 60 min, but the intensity of the (0 0 1) reflection decreases drastically in the XRD pattern of the gel after drying for 80 min. The d-values of the (0 0 1) reflections are closely similar to that of the n-deoxy derivative of HCaNb. The solid-state 27Al CP/MAS NMR spectra of the product after drying for 80 min (not shown) exhibited signals at 18, 22, 27, 30, 33 and 80 ppm due to the n-deoxy groups, 

(Fig. 2(b)) also indicates the occurrence of partial exfoliation.

In the solid-state 29Si NMR spectra (Fig. 3(a)), three signals were detected at −89, −99 and −110 ppm. These signals are assignable to Q^2[SiO]_2Si(0–)g], Q^2[SiO]_3, Si(0–)g] and Q^3[Si(OSi)]_g environments, respectively [18]. These results suggest the formation of a siloxane network via hydrolysis and condensation. With the XRD and TEM results taken into account, the dispersion of nanosheets possessing perovskite-related structures in the siloxane network is clearly demonstrated.

In order to investigate the reaction mechanism, we studied the hydrolysis of TMOS in the presence of the n-octylamine-HCaNb intercalation compound possessing no alkoxy groups on the interlayer surface. The XRD pattern of the product shows a (0 0 1) reflection with d = 3.22 nm, consistent with the interlayer distance of the n-octylamine-HCaNb intercalation compound. The intensity of the (0 0 1) reflection did not decrease, indicating that the n-octylamine-HCaNb intercalation compound cannot react with hydrolyzed TMOS (=SiOH groups). According to an earlier report on a silica-clay nanocomposite,
consistent with the presence of the unreacted $n$-decoxy derivative of HCaNb. In the XRD pattern of the gel after drying for 1 d (Fig. 1(b)), no (0 0 1) reflection due to the unreacted $n$-decoxy derivative of HCaNb is detected. The observed behavior of the (0 0 1) reflection (the decreasing intensity and disappearance of (0 0 1) reflection) during the drying process indicates that a reaction of the $n$-decoxy derivative of HCaNb and siloxane involving exfoliation occurs during the drying process (during change from wet-gel to dry-gel).

We further investigated the changes in the siloxane network structures during the drying process. During the drying process, the volume of the gel decreased drastically between 60 and 80 min. The solid-state $^{29}$Si NMR spectra of the gels after drying for 60 and 80 min show no essential change, however, in the intensity ratio of $Q^2:Q^3:Q^4$ ($=\text{ca. } 0.2:1:0.7$) (Fig. (b) and (c)). These results consequently suggest shrinkage of the siloxane network caused by volatilization of the solvent with no obvious growth of the siloxane network. In the solid-state $^{29}$Si NMR spectrum of the gel after drying for 1 d, the intensity ratio of $Q^2:Q^3:Q^4$ is ca. 0.2:1:1.7; the relative amount of the $Q^4$ environment increases, indicating growth of the siloxane network during the drying process from 80 min to 1 d. Since the (0 0 1) reflection disappears during the drying process from 80 min to 1 d, growth of the siloxane network might affect the exfoliation of HCaNb.

![Fig. 2. TEM images of (a, b) the reaction product of the $n$-decoxy derivative of HCaNb and TMOS after drying for 1 d and (c) the reaction product of the $n$-decoxy derivative of HCaNb and TMOS after freeze-drying.](image)

![Fig. 3. Solid-state $^{29}$Si MAS NMR spectra of the reaction product of the $n$-decoxy derivative of HCaNb and TMOS after drying for (a) 60 min, (b) 80 min and (c) 1 d.](image)
In order to investigate the structure of the gel before the drying process, freeze-drying of the product was conducted instead of drying at 80 °C. The XRD pattern of the gel after freeze-drying shows a reflection at $2\theta = 3.34^\circ$, indicating the presence of a stacking order along the $c$-axis (Fig. 1(f)). In addition, the TEM image of the freeze-dried product (Fig. 2(c)) clearly demonstrates the presence of a stacking order of perovskite-related nanosheets with an interlayer distance of ca. 3.2 nm. These results support the conclusion that a reaction of the $n$-decoxy derivative of HCaNb and TMOS involving exfoliation occurs during the drying process. The proposed model for the exfoliation process is illustrated in Fig. 4.

4. Conclusions

Cohydrolysis of the $n$-decoxy derivative of HCaNb and TMOS was conducted. The XRD, TEM and solid-state $^{29}$Si NMR results clearly showed the formation of a nanocomposite possessing exfoliated nanosheets in the siloxane network. The exfoliation process was also investigated during the drying process. The presence of the unreacted $n$-decoxy derivative of HCaNb was detected by the XRD and solid-state $^{13}$C CP/MAS NMR results for the gel before drying. The XRD patterns of the gels after drying for 60 and 80 min showed that the relative intensity of $(0 0 l)$ reflections decreased with increase in the drying time. The $(0 0 l)$ reflections disappeared in the XRD of the gel after drying for 1 d, indicating that the nanocomposite after drying for 1 d comprised an exfoliated structure. These results indicate that exfoliation occurred during the drying process. It is therefore expected that the use of nanobuilding blocks possessing perovskite-related structures in a sol–gel process with various metal alkoxides will potentially enable us to prepare various nanocomposites possessing nanosheets.

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