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Surface modification of a layered alkali titanate with organosilanes

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Silylated derivatives of $K_2Ti_4O_9{\cdot}nH_2O$ were successfully synthesized by the reaction of octylammonium–tetratitanate intercalation compound with *n*-alkyltrimethoxysilanes.

Organization of organic species on the surface of inorganic solids is a way to prepare inorganic–organic hybrids.[1] Materials design from layered materials through soft-chemical routes is a promising strategy, since the resulting layered inorganic–organic hybrids may have unique nanostructures controlled by host–guest interactions. A wide variety of layered inorganic–organic hybrids have been prepared by intercalation reactions and their properties and possible applications have been investigated.[2] Among possible intercalation reactions, the immobilization of organic units through covalent bonds, such as the silylation of interlayer silanol groups of layered silicates with organosilanes,[3] has merit in practical applications due to the thermal and chemical stabilities of the hybrids. The silylation of layered silicates has resulted in novel hybrid materials with such functions as film-forming abilities[3c] and adsorptive properties.[3d] Accordingly, the application of silylation to the modification of other layered materials is worth investigating.

Layered alkali titanates, niobates and titanoniobates are classes of materials with unique ion exchange and photocatalytic properties. The adsorption of organic cations such as alkylammonium ions[4] and cationic dyes[5] through cation exchange reactions has been reported. However, to our knowledge, there are only a few reports on the covalent attachment of functional units on the surface. The intercalation of organosilanes into layered alkali titanates for the preparation of silica pillared titanate[6] and the reactions of these with a layered niobate[7] and titanoniobate[8] are reported examples. This paper reports the successful silylation of $K_2Ti_4O_9{\cdot}nH_2O$ with alkyltrimethoxysilanes. Nanosheets of layered titanates, niobates, and titanoniobates in aqueous suspensions have been studied as modules to fabricate advanced materials including liquid crystals and thin films.[9] However, to our knowledge, this is the first successful report on the suspension of titania nanosheets in organic solvents.

The silylation was conducted by using the octylammonium–tetratitanate intercalation compound (designated as C_8N^+–Ti_4O_9) as the intermediate. The C_8N^+–Ti_4O_9 was prepared by a one-pot process where $K_2Ti_4O_9{\cdot}nH_2O$[10] (2.0 g) was allowed to react with an aqueous mixture of propylamine (1.2 ml) and octylamine (2.0 ml), whose pH was adjusted to 10 by the addition of 1 M HCl. The reaction was conducted at room temperature for 1 h and the product was separated by centrifugation. The X-ray diffraction (XRD) pattern (Fig. 1b) and the IR spectrum of C_8N^+–Ti_4O_9 were consistent with those reported previously.[4c] From the elemental analysis (Table 1), the amount of intercalated C_8N^+ was determined to be 1.0 mol per $[Ti_4O_9]^{2-}$. All these results indicate the successful formation of C_8N^+–Ti_4O_9 by the present one-pot process. C_8N^+–Ti_4O_9 (0.5 g) was suspended in a mixture of *n*-alkyltrimethoxysilane (8.0–11.0 ml) and toluene (50 ml) and the mixture was allowed to react at 60 °C for 48 h. The product was separated by centrifugation and washed with acetone. The silylated derivatives thus obtained are designated as C_nTMS–Ti_4O_9 (*n* denotes the carbon number in the alkyl chain).

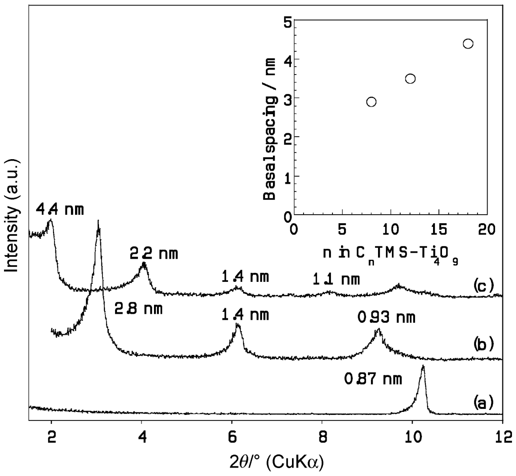

Fig. 1 X-Ray diffraction patterns of (a) $K_2Ti_4O_9{\cdot}nH_2O$, (b) C_8N^+–Ti_4O_9 and (c) C_{18}TMS–Ti_4O_9. Inset: the variation of the basal spacing as a function of alkyl chain length of the organosilyl groups. The *d*(200) values of C_nTMS–Ti_4O_9 are 2.9, 3.5 and 4.4 nm for C_8TMS–Ti_4O_9, C_{12}TMS–Ti_4O_9 and C_{18}TMS–Ti_4O_9, respectively.

The XRD pattern of C_{18}TMS–Ti_4O_9 is shown in Fig. 1c. The *d*(200) value increased upon silylation to 4.4 nm. The IR spectrum of C_{18}TMS–Ti_4O_9 showed absorption bands due to the organosilyl groups, such as the SiO–C stretching vibration at 1092 cm^{-1} and Si–O–Si stretching vibration at 1017 cm^{-1}.[11] The absorption band due to the Si–O–Ti stretching vibration is thought to be hidden by the strong absorption band due to $K_2Ti_4O_9{\cdot}nH_2O$. In the ^{29}Si MAS NMR spectrum of C_{18}TMS–Ti_4O_9, five signals due to silicon atoms in different chemical environments were observed and they were assigned as schematically shown in Fig. 2 inset.[12] The compositions of the silylated derivatives were determined by ICP-AES† and CHN elemental analysis. From the Si and Ti contents, the amount of intercalated organosilyl groups was determined to be 1.0 mol per Ti_4O_9 for C_{18}TMS–Ti_4O_9 (Table 1). The deintercalation of C_8N^+ during the silylation was confirmed by the decreased N content. Similar results were obtained for C_8TMS–Ti_4O_9 and C_{12}TMS–Ti_4O_9 and the results are summarized in Table 1. The expanded interlayer space of C_8N^+–Ti_4O_9 made it possible to introduce bulkyl organosilyl groups into the interlayer space as reported for silylation of layered silicates.[3c–e] The needle-like morphology with an average length of ~4 μm of $K_2Ti_4O_9{\cdot}nH_2O$ did not change upon silylation, as seen by scanning electron microscopy, indicating that the silylation occurred topochemically.

Table 1 Chemical composition of C_8N^+–Ti_4O_9 and he C_nTMS–Ti_4O_9

	C (mass%)	N (mass%)	Si (mass%)	Ti (mass%)	Si/Ti_4O_9 mol
C_8N^+–Ti_4O_9	20.4	2.9	—	52.6	—
C_8TMS–Ti_4O_9	18.0	0.74	4.4	25.8	1.2
C_{12}TMS–Ti_4O_9	22.2	0.75	3.5	28.4	0.84
C_{18}TMS–Ti_4O_9	30.9	0.75	3.4	22.4	1.0

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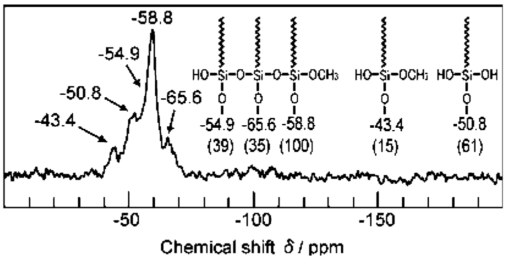

Fig. 2 ^{29}Si MAS NMR spectrum of C_{18}TMS–Ti_4O_9. Parentheses indicate relative intensities of each signal.

The TG-DTA curves of C_{18}TMS–Ti_4O_9 and C_8N^+–Ti_4O_9 recorded under helium are shown in Fig. 3. The DTA curve of C_{18}TMS–Ti_4O_9 showed an endothermic peak due to the decomposition of the attached organosilyl groups starting from 490 °C with *ca.* 22% mass loss in the corresponding TG curve. The thermal decomposition occurred at a higher temperature region if compared with that (100 °C) observed for C_8N^+–Ti_4O_9. Similar thermal decomposition behavior (at around 500 °C) was observed for C_8TMS–Ti_4O_9. The thermal stability is worth mentioning as a merit of the present material design. The gradual mass loss of *ca.* 12% from 160 °C to 490°C in the TG curve of C_{18}TMS–Ti_4O_9 is likely due to the desorption of both the remaining C_8N^+ and the organosilyl groups which are weakly bound or not immobilized on the titanate sheets.

Fig. 1 inset shows the variation of the *d*(200) values of C_nTMS–Ti_4O_9. There is a linear relationship between the carbon number in the alkyl chain and the *d*(200) values. Taking the size of the alkyl groups into consideration (*i.e.* 2.4 nm for the octadecyl groups), the intercalated organosilyl groups were thought to adopt a paraffin-type arrangement in the silylated derivatives. The amount of intercalated organosilyl groups did not depend on the alkyl chain length, maybe due to the configuration of the bulkyl organosilyl groups and/or full occupation of the interlayer titanol groups with the organosilyl groups. The *d*(200) value and the composition (alkyl groups/Ti_4O_9) of the silylated derivatives were consistent with those of the alkylammonium derivatives.[4c] It was thought that the surface titanol groups able to interact with alkylammonium ions were quantitatively reacted with *n*-alkyltrimethoxysilanes.

The attached organosilyl groups could not be removed by washing C_{18}TMS–Ti_4O_9 (10 mg) for 24 h with acetone, chloroform, hydrochloric acid, or aqueous ammonia (50 ml). A decrease of the *d*(200) value (from 4.4 to 3.9 nm) was observed for the product after washing with hydrochloric acid, however, no elution of the organosilyl groups was detected by ICP-AES. The *d*(200) value did not change upon washing with acetone, chloroform, or aqueous ammonia. The IR spectra of the washed product did not show the deintercalation of the organosilyl groups. All these results indicate that the organosilyl groups were stably immobilized on the surface of the titanate sheets. The morphology of the C_{18}TMS–Ti_4O_9 particles did not change upon washing, as seen in the SEM.

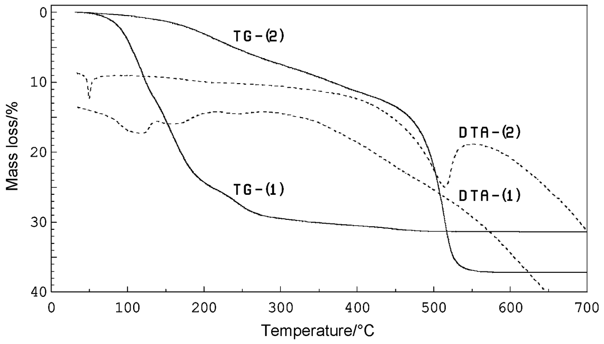

Fig. 3 TG (solid)-DTA (dashed) curves recorded under helium of (1) C_8N^+–Ti_4O_9 and (2) C_{18}TMS–Ti_4O_9.

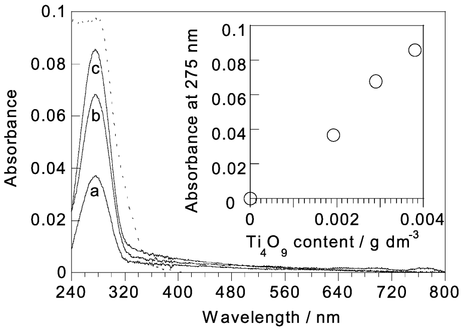

Fig. 4 UV-visible absorption spectra of the colloidal suspensions of C_{18}TMS–Ti_4O_9 at various Ti_4O_9 concentrations: (a) 0.0019, (b) 0.0029, (c) 0.0038 g dm^{-3}. $K_2Ti_4O_9{\cdot}nH_2O$ recorded in diffused reflectance mode is denoted by the dashed trace. Inset: the absorbance at 275 nm as a function of the colloid content.

The silylated derivatives dispersed in toluene, methanol, and chloroform. The UV-visible absorption spectra of translucent suspensions of C_{18}TMS–Ti_4O_9 suspended in chloroform with various concentrations are shown in Fig. 4 together with the diffuse reflectance spectrum of $K_2Ti_4O_9{\cdot}nH_2O$. The well-developed absorption peaks appeared near the absorption onsets and obeyed the Beer–Lambert law. This behavior was consistent with that reported for a colloidal suspension of titania nanosheets prepared by swelling of a layered protonic titanate, $H_xTi_{2-x/4}\square_{x/4}O_4{\cdot}H_2O$ (□: vacancy), with lepidocrocite-type structure and is thus due to the molecular nature of the nanosheets and their size quantization.[13] It is thus suggested that C_{18}TMS–Ti_4O_9 incorporated organic solvents into the organo-modified interlayer space to swell.

The present materials design is applicable to various functional units since a wide variety of organosilanes with different functionalities are available. Further studies on the attachment of functional units are in progress in our laboratory.

Notes and references

† The silylated derivatives (10 mg) were alkali-fused with Na_2CO_3 (0.5 g). The resulting solids were sealed with conc. H_2SO_4 and heated at 150 °C for 2 h to dissolve in water. The transparent solutions thus obtained were used as the sample solutions.

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