Incorporation of Ethylenediamine as a Bi-layer in the Interlayer Space of Tetratitanic Acid by Re-stacking Exfoliated Nanosheets

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The reaction of ethylenediamine with a colloidal suspension containing exfoliated $H_2Ti_4O_9$ nanosheets was studied. Characterization of the product by X-ray diffraction, thermogravimetry-differential thermal analysis, elemental analysis, and solid-state ^{13}C NMR revealed that two types of ethylenediamine–$H_2Ti_4O_9$ intercalation compounds, namely, compounds with ethylenediamine in a mono-layer or a bi-layer arrangement, could be prepared depending on the synthetic conditions. The latter composite material is a novel intercalation compound with the ethylenediamine arranged in a bi-layer with one amine group attached to the interlayer surface of $H_2Ti_4O_9$ as an ammonium cation ($–NH_3^+$) and the other group present in the interlayer space in a neutral state ($–NH_2$).

Various layered inorganic compounds can accommodate organic ions and molecules in the interlayer space to form intercalation compounds, where inorganic layers and organic molecules or ions are interstratified at a molecular level.[1–3] Intercalation compounds are generally prepared via ion-exchange reactions, adsorption based interactions such as acid–base with interlayer cations or surfaces, or modification of the interlayer surface by grafting reactions. The use of exfoliated (delaminated) titanic acid nanosheets[4] for the fabrication of advanced functional materials that are otherwise difficult or cannot be obtained through conventional intercalation reactions has been demonstrated by Sasaki and co-workers[5–12] as well as other groups.[13–17] The successful synthesis of a novel composite of mesoporous structured alumina pillared titanate with a bi-layer arrangement using exfoliated $H_xTi_{2-x/4}\square_{x/4}O_4 \cdot nH_2O$ (□: vacancy) nanosheets[8,9] (conventional intercalation reactions result in a mono-layer arrangement) suggests the possibility of the synthesis of novel composites by re-stacking of nanosheets.

Reports on the introduction of functional groups such as $–NH_2$, –OH, or –COOH groups in the interlayer are limited.[18,19] The reaction of an amino acid, lysine ($NH_2(CH_2)_4CH(NH_2)COOH$), with $HTiNbO_5$ has been reported to result in an intercalation compound with one end of the chain forming a cation $–NH_3^+$ while the other end involves the carboxylic function forming hydrogen bonds with another lysine chain.[18] An alcohol-exchange reaction of an alkoxy modified-layered niobate presents an interesting case where ethylene glycol can be introduced into the interlayer as a bi-layer with the alkyl group bound to the oxide interlayer surface (R–O–Nb) and a free –OH functional group present in the interlayer gallery.[19]

Here we report the re-stacking behavior of exfoliated titanic acid nanosheets upon reaction with ethylenediamine. $H_2Ti_4O_9 \cdot nH_2O$, so-called tetratitanic acid, was chosen as the host oxide since its exfoliation behavior[17] as well as the intercalation of alkylamines and alkyldiamines have been reported.[20–22] Airoldi et al.[21] reported that the direct reaction of $H_2Ti_4O_9 \cdot nH_2O$ with aqueous alkyldiamines resulted in intercalation compounds with alkyldiamine arranged in a mono-layer and the amine groups attached to the tetratitanic acid sheets as ammonium cations. Here, we will demonstrate that the reaction of ethylenediamine with exfoliated tetratitanic acid nanosheets results in a novel intercalation compound with alkyldiamine present in a bi-layer arrangement in the interlayer gallery.

Experimental

A colloidal suspension containing exfoliated tetratitanic acid nanosheets was obtained by suspending a tetrabutylammonium–$H_2Ti_4O_9 \cdot nH_2O$ intercalation compound in methanol.[17] The protonated tetratitanate, $H_2Ti_4O_9 \cdot nH_2O$, was prepared by acid treatment of fibrous $K_2Ti_4O_9 \cdot nH_2O$ (courtesy of Ohtsuka Chemicals). The ethylammonium–$H_2Ti_4O_9 \cdot nH_2O$ intercalation compound was prepared by the reaction of room temperature-dried $H_2Ti_4O_9 \cdot nH_2O$ with aqueous solutions of ethylamine for 24 h at room temperature. The ethylammonium–$H_2Ti_4O_9 \cdot nH_2O$ intercalation compound was allowed to react with aqueous solutions of tetrabutylammonium hydroxide at room temperature for 50 h, followed by centrifugal collection at 15000 rpm. The particulate product was subsequently suspended in methanol. Relatively large particles and agglomerates were centrifugally separated at 2000 rpm. The colloidal supernatant containing exfoliated tetratitanic acid nanosheets was used for further investigation. The concentration of the tetratitanic acid was approximately 0.7 grams of TiO_2 per liter of CH_3OH. Ethylenediamine was added to the colloidal suspension containing exfoliated tetratitanic acid nanosheets in the following ratios: $[\text{ethylenediamine}]/[H_2Ti_4O_9] = 1.2$, 7.5, 13, 68, and 200. Ethylenediamine was dissolved in methanol in a separate pot with various concentrations (0.7, 3.3, 7.0, 33.0 vol %) and added to the colloidal suspension. Neat ethylenediamine was reacted likewise with the colloidal suspension. After magnetic stirring for 7 h to ensure complete reaction, the precipitate was centrifugally collected at 15000 rpm for characterization.

The structure of the air-dried products was studied by X-ray diffraction (XRD) (Rigaku RINT 2550H/PC; monochromated

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Cu Kα radiation). Thermal gravimetry/differential thermal analysis (TG/DTA) was conducted with a Rigaku TAS-200 under a flow of dry air. The heating rate was 10 °C min^{-1} and α-Al_2O_3 was used as a standard. Elemental analysis was performed on a Perkin-Elmer Series II CHNS/O Analyzer 2400. Solid-state ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer with dipole decoupled MAS techniques (DD/MAS) at 100.13 MHz. Samples were spun at a frequency of 5 kHz at the magic angle (54.7°) with respect to the static magnetic field. The 90° pulse width was 3 µs and the recycle delay was set to 30 s. Chemical shifts are reported with respect to external TMS. Field-emission scanning-electron microscopy (FE-SEM) (Hitachi S-5000) was utilized for morphological observation of the products.

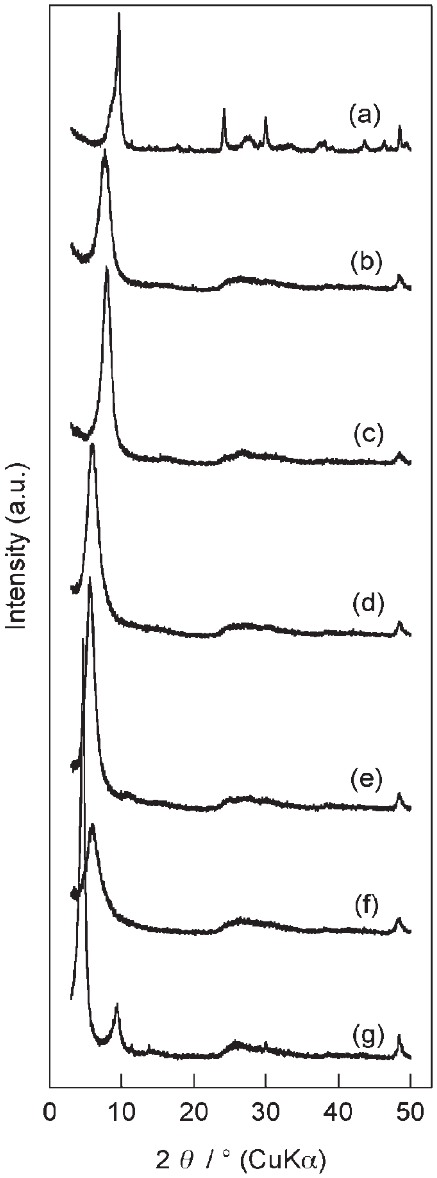

Fig. 1. (a) XRD patterns of $H_2Ti_4O_9 \cdot nH_2O$, the products obtained by the reaction of exfoliated tetratitanic acid nanosheets and ethylenediamine with [ethylenediamine]/[$H_2Ti_4O_9$] = (b) 1.2, (c) 7.5, (d) 13, (e) 68, (f) 200, and (g) tetrabutylammonium–tetratitanic acid intercalation compound.

Results and Discussion

The X-ray diffraction (XRD) patterns of the products obtained by reacting exfoliated tetratitanic acid nanosheets with various amounts of ethylenediamine ([ethylenediamine]/[$H_2Ti_4O_9$] = 1.2, 7.5, 13, 68, 200) are shown in Fig. 1. The XRD patterns of $H_2Ti_4O_9 \cdot nH_2O$ and the tetrabutylammonium–$H_2Ti_4O_9$ intercalation compound are also shown. The XRD patterns of all of the samples revealed that the (020) reflection at $2\theta = 48.5°$, characteristic of the in-plane structure, was unchanged. This indicates that the layered structure was preserved for all of the products. The basal spacings of the products obtained with [ethylenediamine]/[$H_2Ti_4O_9$] = 1.2 and 7.5 were $d = 1.14$ and 1.12 nm. These values are smaller than the basal spacing of the tetrabutylammonium–$H_2Ti_4O_9$ intercalation compound ($d = 1.87$ nm) suggesting an exchange in the interlayer species. The d value is comparable to that obtained from the direct reaction of ethylenediamine with $H_2Ti_4O_9 \cdot nH_2O$ ($d = 1.12$ nm).[21] The interlayer distance, $d_{\text{interlayer}}$, of the products can be estimated from the equation, where $\alpha \sim 104°$ and $d_{\text{oxide sheet}} \sim 0.56$ nm based on a previous study.[23] The basal spacing of $d \sim 1.1$ nm gives an interlayer distance of ~0.5 nm, which is close to the geometric size of ethylenediamine (~0.4 nm).

The reaction of exfoliated tetratitanic acid with higher ethylenediamine concentrations ([ethylenediamine]/[$H_2Ti_4O_9$] $\geq$ 13) resulted in products with a larger basal spacing of $d =$ 1.48–1.54 nm. The basal spacing of $d \sim 1.5$ nm translates to an interlayer distance of 0.9 nm. This value is too large to assume a mono-layer arrangement, considering the geometric size of ethylenediamine (~0.4 nm).

The TG curves of the products obtained by the reaction with [ethylenediamine]/[$H_2Ti_4O_9$] = 1.2 (hereafter denoted as en-HTOns(I)) and with [ethylenediamine]/[$H_2Ti_4O_9$] = 200 (hereafter denoted as en-HTOns(II)) are shown in Fig. 2.

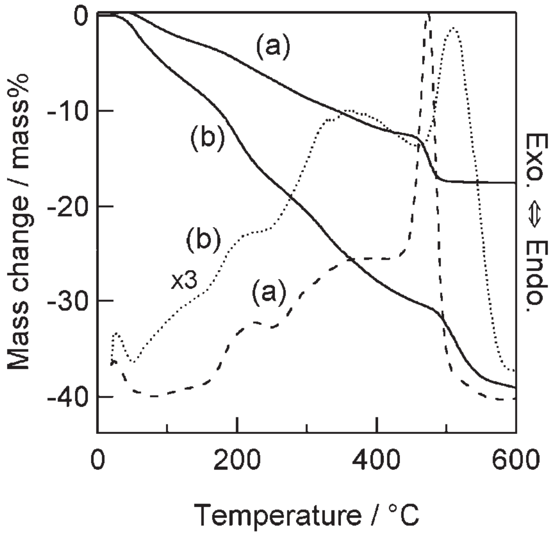

Fig. 2. TG (lines) and DTA (broken lines) curves of the products obtained by the reaction of exfoliated tetratitanic acid nanosheets and ethylenediamine with [ethylenediamine]/[$H_2Ti_4O_9$] = (a) 1.2 (en-HTOns(I)) and (b) 200 (en-HTOns(II)).

The TG curves of en-HTOns(I) and en-HTOns(II) showed mass losses of 14 and 30 mass% between 160 and 600 °C, respectively. The atomic ratios based on elemental analysis for en-HTOns(I) and en-HTOns(II) were C:H:N = 6:2:4 and 9:3:7 respectively. Based on the above results, the ethylenediamine content for en-HTOns(I) is approximately 0.5 moles $H_2NC_2H_4NH_2$ per Ti_4O_9 and 1.0 mole $H_2NC_2H_4NH_2$ per Ti_4O_9 for en-HTOns(II). The elemental analysis data also shows that the products contain about 0.1 mole tetrabutylammonium per Ti_4O_9.

The DTA curves for en-HTOns(I) and en-HTOns(II) (Fig. 2) exhibit multiple exothermic peaks due to the decomposition of the organic species. There is no significant difference in the decomposition process between the two samples up to 400 °C. However, a noticeable difference was observed above 400 °C: the last exothermic reaction for en-HTOns(II) was observed at higher temperature than en-HTOns(I), suggesting a different interlayer environment.

Further evidence of the different interlayer environment of en-HTOns(I) and en-HTOns(II) was obtained by solid-state ^{13}C NMR studies, as shown in Fig. 3. A signal assignable to the CH_2 group appeared at 39 ppm for en-HTOns(I). In the case of en-HTOns(II) the CH_2 group appeared at 42 ppm. The weak signals marked with asterisks in Fig. 3(a) can be attributed to the tetrabutyl group of tetrabutylammonium.

Besides the difference in the interlayer environment, scanning electron microscopy revealed that the textures of en-HTOns(I) and en-HTOns(II) were also different (Fig. 4). The micrograph for en-HTOns(II) shows a porous structure consisting of agglomerates of flaky particulates, similar to the morphology of porous $H_xTi_{2-x/4}\square_{x/4}O_4 \cdot nH_2O$ obtained via an exfoliation–restacking–freeze drying process.[5]

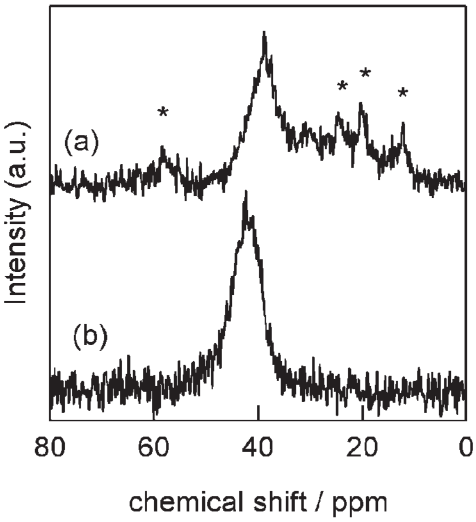

Fig. 3. Solid-state ^{13}C NMR spectra of the products obtained by the reaction of exfoliated tetratitanic acid nanosheets and ethylenediamine with [ethylenediamine]/[$H_2Ti_4O_9$] = (a) 1.2 (en-HTOns(I)) and (b) 200 (en-HTOns(II)). The signals marked with asterisks in (a) are due to residual tetrabutylammonium.

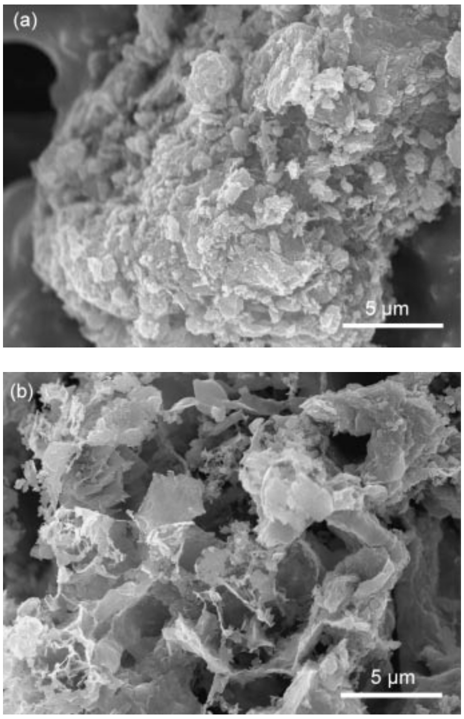

Fig. 4. Typical SEM images of the products obtained by the reaction of exfoliated tetratitanic acid nanosheets and ethylenediamine with [ethylenediamine]/[$H_2Ti_4O_9$] = (a) 1.2 (en-HTOns(I)) and (b) 200 (en-HTOns(II)).

The results show that en-HTOns(I) and en-HTOns(II) have noticeably different interlayer environments and texture. The interlayer distance and organic content of en-HTOns(II) suggests that ethylenediamine is present as a bi-layer in the interlayer. The overall composition of en-HTOns(II) can be approximated[24] as $(H_2NC_2H_4NH_2)_{1.0}H^+{}_{2.0}[Ti_4O_9]^{2-}$, $(H_2NC_2H_4N^+H_3)_{1.0}H^+{}_{1.0}[Ti_4O_9]^{2-}$, or $(H_3N^+C_2H_4N^+H_3)_{1.0}$-$[Ti_4O_9]^{2-}$ depending on the charged state of the amine group (neutral, monovalent, or divalent). The last composition with both amine in the charged state ($-NH_3^+$) would be unlikely because of the repulsion between the positive charges in a bi-layer arrangement. IR spectroscopy revealed the presence of both NH_2 and NH_3^+ in en-HTOns(II) (3170 cm^{-1}, ν(N–H); 1620 cm^{-1}, δ($-NH_2$); 1510 cm^{-1}, δ($-NH_3$). Hence, the most probable composition for en-HTOns(II) is $(H_2NC_2H_4N^+H_3)_{1.0}$-$H^+{}_{1.0}[Ti_4O_9]^{2-}$, where one $-NH_3^+$ group is attached to the interlayer surface of the tetratitanic acid and one $-NH_2$ functional group is present in the interlayer space.

In the case of en-HTOns(I), the interlayer distance suggests that ethylenediamine may be present in the interlayer as a mono-layer or a strongly inclined bi-layer. The DTA and NMR data show that the interlayer environment of en-HTOns(I) and en-HTOns(II) were different and the SEM images show that the re-stacking process is also quite different. Hence, we believe that ethylenediamine in en-HTOns(I) is present as a mono-layer in the interlayer with both amine groups present as $-NH_3^+$ attached to the oxide surface, in contrast to the bi-layer arrangement in en-HTOns(II). The difference in the chemical shift observed in the solid-state ^{13}C NMR spectrum is thus suggested to arise from the difference in the charged state of the amine groups, that is $H_3N^+C_2H_4N^+H_3$ for en-HTOns(I) and $H_2NC_2H_4N^+H_3$ for en-HTOns(II).

Since one $-NH_3^+$ group is attached to the interlayer surface of the tetratitanic acid and one $-NH_2$ functional group is pres-

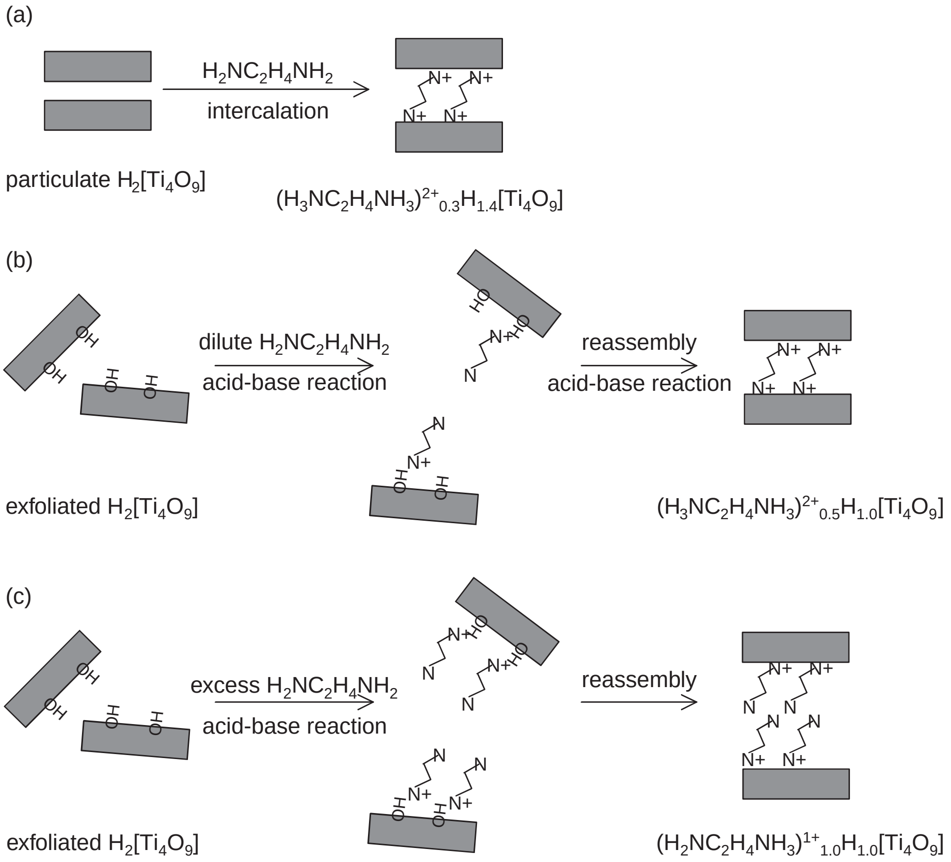

Fig. 5. (a) Schematic representation of an ethylenediamine–tetratitanic acid intercalation compound obtained by a conventional intercalation reaction. The proposed reaction scheme[24] for the ethylenediamine–tetratitanic acid intercalation compound obtained by the reaction of exfoliated tetratitanic acid nanosheets and ethylenediamine with (b) [ethylenediamine]/[$H_2Ti_4O_9$] $\leq$ 7.5, and (c) [ethylenediamine]/[$H_2Ti_4O_9$] $\geq$ 13.

ent in the interlayer space in en-HTOns(II), we propose that the acid–base type reaction between ethylenediamine and exfoliated tetratitanic acid nanosheets occurs first via an acid–base reaction between one of the amine groups in ethylenediamine and the surface OH group of an exfoliated tetratitanic acid nanosheet, as schematically illustrated in Fig. 5. If ethylenediamine were to be itself protonated into ethylenediammonium, a bi-layer arrangement would be unlikely. Under conditions where only a small amount of ethylenediamine is present, as in the case of en-HTOns(I), the remaining amine group in ethylenediamine will further react with the accessible surface OH group of a nearby exfolaited tetratitanic acid nanosheet via an acid–base reaction (Fig. 5b). When ethylenediamine is present in excess, ethylenediamine will react with all of the accesible surface OH groups of an exfoliated tetratitanic acid nanosheet via an acid–base reaction (Fig. 5c). The re-stacking of the ethylenediamine-modified exfoliated tetratitanic acid nanosheets will occur via interaction between the $-C_2H_4NH_2$ covering the surface of exfoliated tetratitanic acid or forced by centrifugation at 15000 rpm. The difference between the strength in the interaction of the second reaction step is most likely the reason for the difference in the morphology of en-HTOns(I) and en-HTOns(II). That is, the acid–base reaction between $-C_2H_4NH_2$ and the accesible surface OH groups of exfoliated tetratitanic acid nanosheets will be strong, while the interactions beween two $-C_2H_4NH_2$ on the surface of exfoliated tetratitanic acid nanosheets will be weak, leading to a porous flaky texture.

The unique inorganic–organic composite obtained by the present re-stacking process of exfoliated tetratitanic acid nanosheets may be relevant to other organic molecules with multifunctional groups as well as other exfoliated oxide systems. The present preparation technique utilizing exfoliated nanosheets should provide a wide range of inorganic–organic composites based on the variety of “modules” that can be used (e.g., inorganic nanosheets based on Ti, Nb, Ta, Mn, etc. and organic compounds with multi-functional groups such as $-NH_2$, –OH, –COOH, –CN, –SH, etc.). Such reactive groups within the interlayer space should be functional for further chemical reactions to afford novel inorganic–organic compounds.

Conclusion

We have successfully prepared a novel intercalation compound where ethylenediamine is present in the interlayer of tetratitanic acid in a bi-layer arrangement. This has been achieved by re-stacking exfoliated tetratitanic acid nanosheets in the presence of ethylenediamine. The resulting ethylenediamine–tetratitanic acid intercalation compound had a porous texture and possessed amine functional groups in the interlayer space. An ethylenediamine–tetratitanic acid intercalation compound with dilute ethylenediamine had a structure similar to the ethylenediamine–tetratitanic acid intercalation compound obtained by conventional intercalation reactions, with ethylenediammonium present as a mono-layer in the interlayer space.

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