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Electrophoretic deposition of negatively charged tetratitanate nanosheets and transformation into preferentially oriented TiO_2(B) film

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A tetrabutylammonium–$H_2Ti_4O_9{\cdot}xH_2O$ intercalation compound was obtained by a guest exchange reaction between tetrabutylammonium hydroxide and an ethylammonium–$H_2Ti_4O_9{\cdot}xH_2O$ intercalation compound, and its dispersion state in aqueous and non-aqueous solutions were studied. Spontaneous exfoliation of $H_2Ti_4O_9{\cdot}xH_2O$ into colloidal nanosheets occurred when the tetrabutylammonium–$H_2Ti_4O_9{\cdot}xH_2O$ intercalation compound was dispersed in water, methyl alcohol, isopropyl alcohol, acetonitrile, *N*,*N*-dimethylformamide, dimethyl sulfoxide, and propylene carbonate, while exfoliation did not occur in tetrahydrofuran. A tetrabutylammonium–$H_2Ti_4O_9{\cdot}xH_2O$ film was obtained by a reassembly process by casting the colloidal suspension containing exfoliated nanosheets, while a $H_2Ti_4O_9{\cdot}xH_2O$ film was directly obtained by electrophoretic deposition. Thermal treatment of the electrophoretically deposited film led to an oriented TiO_2(B) film with the (0*k*0) planes lying perpendicular to the substrate.

Introduction

A variety of layered titanates react with organic species to form intercalation compounds. The reaction of certain alkylamines with layered titanates possessing lepidocrocite-type structure ($H_{0.67}Ti_{1.83}\square_{0.17}O_4{\cdot}xH_2O$)[1–18] and Ruddlesden–Popper type structure ($H_2La_2Ti_3O_{10}{\cdot}xH_2O$)[19] leads to delamination of the titanate layers into multilamellar or unilamellar nanosheets in a process known as exfoliation. Such nanosheets are promising material for photofunctional material,[6–8] and have been utilized as building blocks for pillared materials,[9–12] inorganic–organic composites,[13,14] and thin films.[15–19] Thin films using exfoliated nanosheets can be fabricated by spin-coating,[15–18] or self-assembly on functionalized substrates.[19] The latter method utilizes the electrostatic interaction of the negatively-charged nanosheets for the self-assembly of exfoliated nanosheets.[19]

Electrophoretic deposition (EPD) is a well-known technique for obtaining highly uniform films of varying thickness.[20,21] EPD is based on the electrophoresis of charged particles under the influence of an electric field. Since EPD makes use of the charge of particles for deposition, it is similar to the electrostatic-assembly method. Uniform films from water-swollen clay[22–25] and exfoliated-cuprate superconductors[26] have been fabricated by EPD. The use of EPD for film processing of layered titanates has recently been reported.[27,28] Kim *et al.* briefly reported on the fabrication of $Bi_4Ti_3O_{12}$ films by EPD using exfoliated $Bi_4Ti_3O_{12}$ which was prepared by an "explosive exfoliation" mechanism.[27] Matsumoto *et al.* reported that the EPD of $H_{0.67}Ti_{1.83}\square_{0.17}O_4{\cdot}xH_2O$ suspended in ethanol–H_2O affords *b*-axis oriented $H_{0.67}Ti_{1.83}\square_{0.17}O_4{\cdot}xH_2O$ films, while that suspended in *n*-alkylamine–H_2O affords *n*-alkylamine-intercalated $H_{0.67}Ti_{1.83}\square_{0.17}O_4{\cdot}xH_2O$ films.[28]

In this study, we examined the exfoliation and EPD of a protonated form of layered tetratitanate, $H_2Ti_4O_9{\cdot}xH_2O$. $H_2Ti_4O_9{\cdot}xH_2O$ is the $n = 4$ member of the layered titanate series with the formula $H_2Ti_nO_{2n+1}{\cdot}xH_2O$ ($3 \leqslant n \leqslant 6$) and possesses double ReO_3-type chains in which the octahedra share their edges. The ion-exchange, intercalation, photochemical, and photocatalytic properties of $H_2Ti_4O_9{\cdot}xH_2O$ have been studied.[29–47] In addition to such properties, $H_2Ti_4O_9{\cdot}xH_2O$ is known as the precursor for monoclinic TiO_2, known as TiO_2(B).[48–54] TiO_2(B) possesses unique electrochemical and catalytic properties compared to other TiO_2 polymorphs.[55–60] A possible reason for the unique properties of TiO_2(B) is that it possesses a lower density compared to anatase and rutile, which provides cavities and channels for improved insertion and transport of hydrogen or small cations.[56,61] TiO_2(B) is a metastable form of titanium dioxide which is obtained *via* the so-called "soft chemistry reaction" involving a low-energy transformation of $H_2Ti_4O_9{\cdot}xH_2O$ into TiO_2(B) upon thermal treatment. Such a distinctive synthetic method has so far been limited to the preparation of TiO_2(B) only in a powder form.

We report here, the exfoliation of $H_2Ti_4O_9{\cdot}xH_2O$ in various solvents, the fabrication of a $H_2Ti_4O_9{\cdot}xH_2O$ film by EPD, and its transformation into a TiO_2 film. We have found that electrophoretic deposition affords fabrication of a $H_2Ti_4O_9{\cdot}xH_2O$ film without an organic cation in the interlayer which allows straightforward conversion into an oriented TiO_2(B) film with the (0*k*0) plane perpendicular to the substrate.

Experimental

The protonated tetratitanate, $H_2Ti_4O_9{\cdot}xH_2O$ was prepared following a previously reported procedure.[31] The ethylammonium–$H_2Ti_4O_9{\cdot}xH_2O$ (EA–$H_2Ti_4O_9{\cdot}xH_2O$) intercalation compound was prepared by the reaction of $H_2Ti_4O_9{\cdot}xH_2O$ with aqueous solutions of *n*-ethylammonium for 24 h at room temperature. EA–$H_2Ti_4O_9{\cdot}xH_2O$ (dried overnight at 120 °C) was allowed to react with aqueous solutions of tetrabutylammonium hydroxide (TBAOH) at room temperature for 50 h followed by centrifugal collection at 15 000 rpm. The particulate product was subsequently suspended in

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various solvents (distilled water, methyl alcohol, isopropyl alcohol, acetonitrile, *N*,*N*-dimethylformamide, dimethyl sulfoxide, propylene carbonate, and tetrahydrofuran). Relatively large particles and agglomerates were centrifugally separated at 2 000 rpm. The supernatant was used for further investigation.

The electrochemical cell for the electrophoretic deposition (EPD) was composed of a Pt plate anode (1 cm^2), a Pt plate cathode (6 cm^2), and a Ag/AgCl reference electrode. The anode and cathode were placed parallel with a separation of 20 mm. EPD was carried out by applying a constant potential of 10 V (*vs.* Ag/AgCl) for 1 minute at 25 °C. Thermal treatment of the deposited films was conducted at 500 °C for 1 h in air.

The structures of the products were studied by X-ray diffraction (XRD) (Rigaku RINT 2550H/PC; monochromated Cu-Kα radiation). Thermal analysis was conducted with a Rigaku TAS-200. Field-emission scanning-electron microscopy (FE-SEM) (Hitachi S-5000) was utilized for morphological observation of the products. In order to observe the morphology of the non-conducting colloidal particles at high magnification without the assistance of metal coatings, which is often used to suppress the effect of charge-up, the colloidal particles were supported on carbon materials (coconut shell activated carbon and Ketjen Black; supplied by Mitsubishi Chemicals).

Results and discussion

The XRD pattern of the product obtained by the reaction of EA–$H_2Ti_4O_9 \cdot xH_2O$ and aqueous TBAOH is shown in Fig. 1. The basal spacing increased from d = 0.98 nm for EA–$H_2Ti_4O_9 \cdot xH_2O$ to d = 1.8 nm. The interlayer distance, $d_{\mathrm{interlayer}}$, of the product was estimated using the following equation:

$$d_{\mathrm{interlayer}} = d_{(200)} \times \sin\alpha - d_{\mathrm{oxide\ sheet}} = 1.2\ \mathrm{nm}$$

where, the values α = 104° and $d_{\mathrm{oxide\ sheet}}$ = 0.56 nm were used based on previous studies.[47] The interlayer distance of 1.2 nm is approximately equal to the geometric size of the TBA ion,[4] suggesting a monolayer arrangement in the interlayer. Analysis of the organic content in the product by thermogravimetry indicated a loss of 22.7 mass% which corresponds to the chemical formula $TBA_{0.3}H_{1.7}[Ti_4O_9]$. These results reveal that ethylammonium in the interlayer was exchanged with tetrabutylammonium to form a tetrabutylammonium–$H_2Ti_4O_9 \cdot xH_2O$ (TBA–$H_2Ti_4O_9 \cdot xH_2O$) intercalation compound.

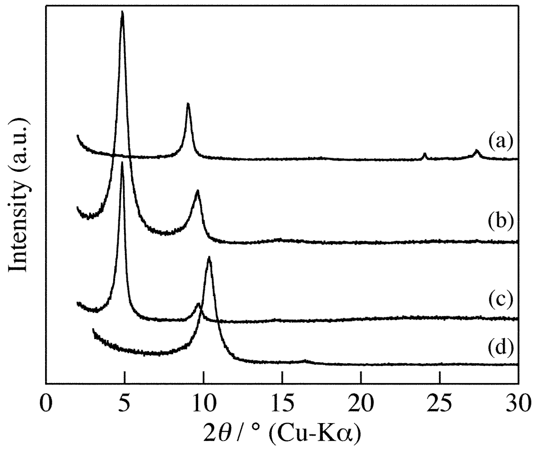


Fig. 1 The XRD patterns of (a) the EA–$H_2Ti_4O_9 \cdot xH_2O$ intercalation compound, (b) the product obtained by the reaction of aqueous TBAOH with EA–$H_2Ti_4O_9 \cdot xH_2O$, (c) a film obtained by casting a colloidal suspension of the product obtained in (b), and (d) a film obtained by electrophoretic deposition of a colloidal suspension of the product obtained in (b).

Dispersion of the TBA–$H_2Ti_4O_9 \cdot xH_2O$ intercalation compound in methyl alcohol resulted in a translucent colloidal suspension that was stable for periods of months. The XRD pattern of a film obtained by casting the colloidal suspension in methyl alcohol onto a glass substrate is shown in Fig. 1c. The XRD pattern of the cast film was identical to that of the TBA–$H_2Ti_4O_9 \cdot xH_2O$ intercalation compound in powder form, which indicates that casting the colloidal solution results in reassembly of the TBA ions and exfoliated $H_2Ti_4O_9 \cdot xH_2O$. Fig. 2 shows the morphology of the exfoliated $H_2Ti_4O_9 \cdot xH_2O$ supported on various carbon materials observed by FE-SEM. Even with the oxide loading, the morphology of the carbon support could be observed, which shows that the oxide sheets have a high degree of flexibility. The oxide sheets have lateral dimensions in the range of approximately 0.1 × 1 μm and thicknesses in the order of nanometers. The FE-SEM image of montmorillonite, a well-known water swellable clay, is also shown for comparison. The FE-SEM images show that the exfoliated nanosheets have a similar morphology to that of swollen clay.

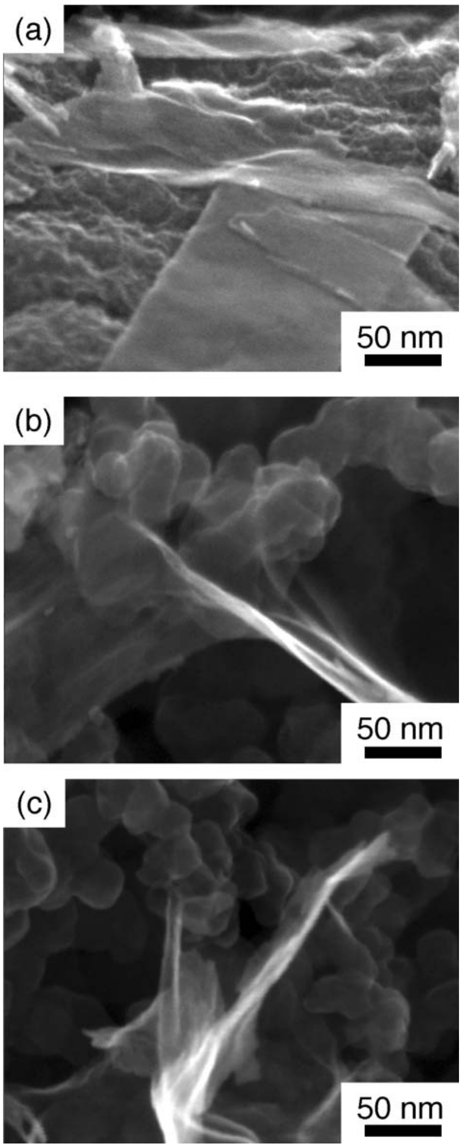


Fig. 2 Typical FE-SEM images of exfoliated $H_2Ti_4O_9 \cdot xH_2O$ supported on (a) coconut-shell based carbon and (b) Ketjen Black. (c) A typical FE-SEM image of montmorillonite supported on Ketjen Black.

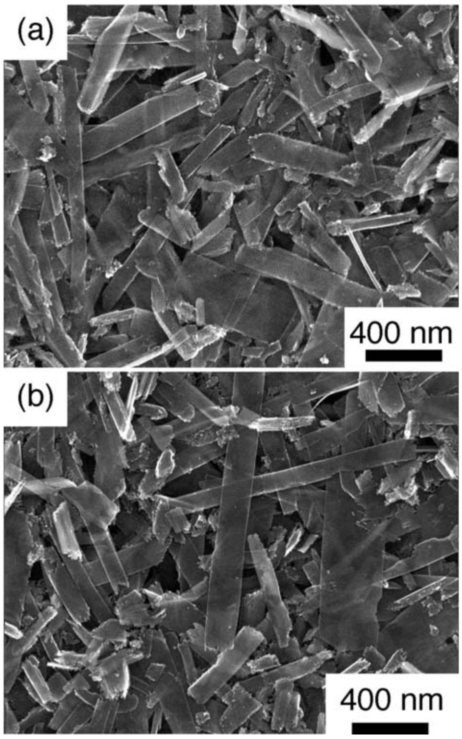


Fig. 3 (a) A typical FE-SEM image of the surface of a film obtained by the EPD from colloidal suspensions of exfoliated $H_2Ti_4O_9{\cdot}xH_2O$. (b) A typical FE-SEM image of a TiO_2(B) film prepared by 500°C treatment of exfoliated $H_2Ti_4O_9{\cdot}xH_2O$.

Table 1 Summary of the properties of the solvents used for the dispersion of TBA–$H_2Ti_4O_9{\cdot}xH_2O$[a]

Solvent	Boiling point/°C	Viscosity[b]/ mPa s	Relative permittivity[b]
Water	99.97	0.890	78.30
Methyl alcohol	64.7	0.545	32.7
Isoproyl alcohol	82.3	1.765_{30}	19.9
Acetonitrile	81.6	0.325_{30}	37.5_{20}
Dimethyl sulfoxide	189.0	2.00	46.7
N,*N*-Dimethylformamide	153.0	0.802	36.7
Propylene carbonate	241.7	2.53	64.4
Tetrahydrofuran	66	0.460	1.75

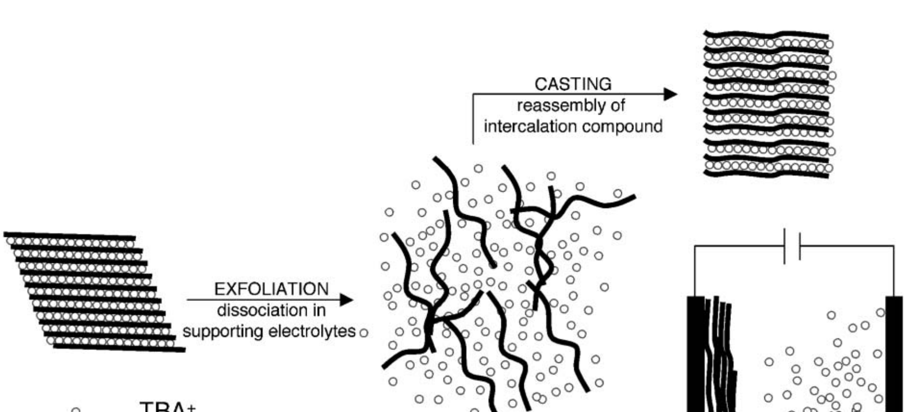
[a] Data from ref. 62. [b] Values are those at 25 °C unless indicated otherwise by the temperatures given as subscripts.

Applying a bias between two electrodes placed in the colloidal suspension of TBA–$H_2Ti_4O_9{\cdot}xH_2O$ in methyl alcohol resulted in deposition at the anode. The film thickness increased as a function of the deposition time; the thickness of the deposited film was 0.6 ± 0.2, 1.4 ± 0.4, and 3.0 ± 0.5 μm for deposition times of 0.5, 1, and 3 minutes, respectively.

A typical FE-SEM image of the surface of a film obtained by the EPD of exfoliated $H_2Ti_4O_9{\cdot}xH_2O$ is shown in Fig. 3, revealing plate-like sheets uniformly stacked parallel to the substrate. Whereas casting the colloidal suspension onto a glass substrate resulted in a TBA–$H_2Ti_4O_9{\cdot}xH_2O$ intercalation compound (Fig. 1c), the XRD pattern of the EPD film (dried overnight at 120°C) was identified as $H_2Ti_4O_9{\cdot}xH_2O$ (Fig. 1d). This suggests that EPD resulted in electrophoresis of the negatively charged exfoliated nanosheets ($[H_{1.7}Ti_4O_9]^{0.3-}{}_{\infty}$) to the anode and the positively charged TBA ions to the cathode. That is, the TBA–$H_2Ti_4O_9{\cdot}xH_2O$ intercalation compound completely dissociates in methyl alcohol, allowing TBA–$H_2Ti_4O_9{\cdot}xH_2O$ to act as an electrolyte and methyl alcohol to act as the supporting electrolyte. This was further supported by studying the stability of the colloidal suspension in various solvents (distilled water, isopropyl alcohol, acetonitrile, *N*,*N*-dimethylformamide, dimethyl sulfoxide, propylene carbonate, and tetrahydrofuran). Stable colloidal solutions were obtained for all the electrolytes with the exception of tetrahydrofuran. The relative permittivity of tetrahydrofuran is too low to act as a supporting electrolyte for the dissociation of negatively-charged titanate sheets and positively-charged TBA ions (Table 1). A proposed mechanism is shown in Scheme 1.

These results differ from that of the EPD of $H_{0.67}Ti_{1.83}\square_{0.17}O_4{\cdot}xH_2O$ suspended in aqueous *n*-alkylamine which resulted in the deposition of the *n*-alkylammonium–$H_{0.67}Ti_{1.83}\square_{0.17}O_4{\cdot}xH_2O$ intercalation compound.[28] Domen *et al.* have reported that the reaction of $H_{0.67}Ti_{1.83}\square_{0.17}O_4{\cdot}xH_2O$ with aqueous ethylamine solution does not lead to delamination into unilamellar sheets, but partial delamination into 10–15 layer multilamellar sheets.[17] Hence, the EPD of $H_{0.67}Ti_{1.83}\square_{0.17}O_4{\cdot}xH_2O$ suspended in aqueous *n*-alkylamine probably led to the deposition of partially delaminated, multilamellar *n*-alkylamine–$H_{0.67}Ti_{1.83}\square_{0.17}O_4{\cdot}xH_2O$ intercalation compound. Bulky cations such as tetrabutylammonium are probably favorable for the complete delamination to unilamellar sheets.

The XRD pattern of the EPD film after thermal treatment at 500 °C is shown in Fig. 4. The XRD pattern closely



Scheme 1 Schematic of the exfoliation and deposition of $H_2Ti_4O_9{\cdot}xH_2O$.

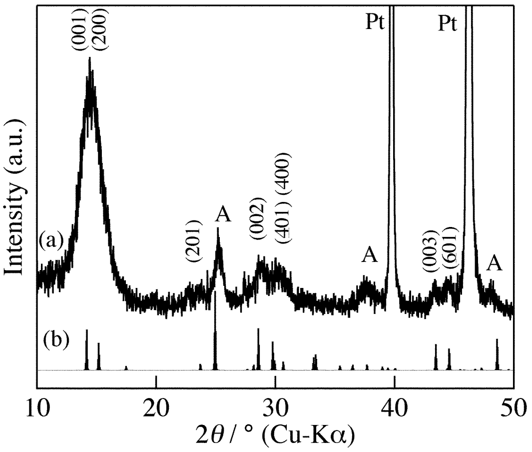


Fig. 4 (a) The XRD pattern of electrophoretically deposited film after thermal treatment at 500 °C and (b) the simulated XRD pattern of $TiO_2(B)$ using the parameters reported by Fiest and Davies (ref. 53). Anatase impurities are marked with an A.

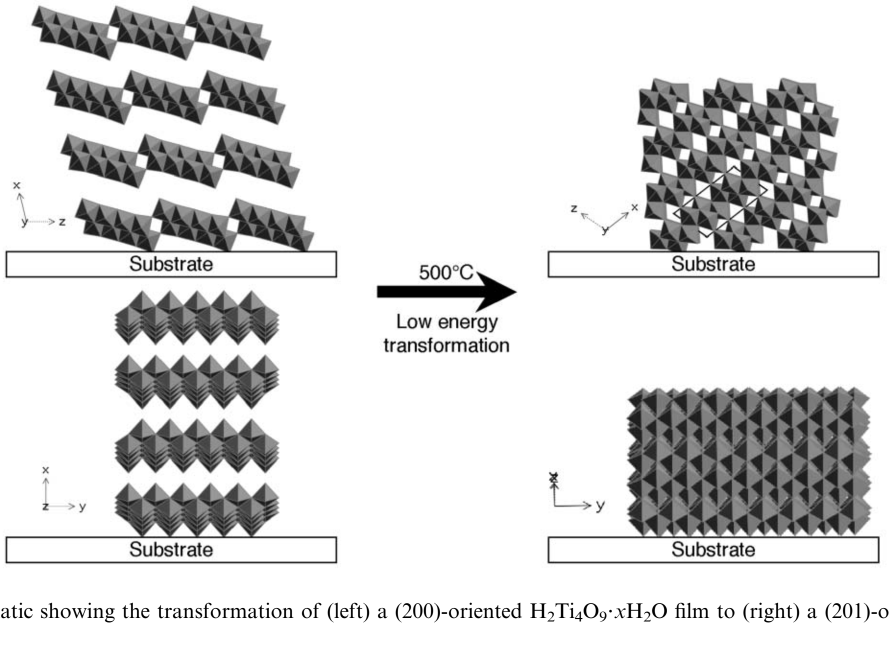
matched that of $TiO_2(B)$, except for the fact that only the ($h0l$) reflections were observed; that is, (110), (310), ($\bar{3}11$), (020) were not observed at $2\theta = 25.0$, 33.2, 33.4, 48.6°. Some weak reflections due to anatase were also observed, but this impurity is very difficult to avoid even by careful optimization of the conditions for thermal treatment.[53] The absence of (hkl) reflections with $k \neq 0$ indicates that $TiO_2(B)$ is oriented with the ($0k0$) planes lying perpendicular to the substrate. As shown in Fig. 3b, the plate-like morphology of the as-deposited films was preserved in the film treated at 500 °C. Hence, the preferred orientation of $TiO_2(B)$ must be related to the *a*-axis orientation of the as-deposited $H_2Ti_4O_9{\cdot}xH_2O$ film.

The transformation of $H_2Ti_4O_9{\cdot}xH_2O$ to $TiO_2(B)$ has been thoroughly discussed by Fiest and Davis.[53] The transformation is not a simple condensation of the interlayer hydroxy groups, and involves a low energy transformation with several transition steps. Based on the above results and the structural similarity between $H_2Ti_4O_9{\cdot}xH_2O$ and $TiO_2(B)$, it can be said that a (201)-oriented $TiO_2(B)$ film was derived from an *a*-axis oriented $H_2Ti_4O_9{\cdot}xH_2O$ film as shown schematically in Scheme 2. The present results indicate that the transformation of $H_2Ti_4O_9{\cdot}xH_2O$ into $TiO_2(B)$ is of low enough energy that the morphology and preferred orientation of the precursor layered tetratitanate is reflected in the resulting $TiO_2(B)$ film. Thermal treatment at 700°C leads to a breakdown of the sheets into 20–30 nm sized anatase particles.

Finally, it should be noted that $TiO_2(B)$ was not observed in the XRD patterns when a cast film using exfoliated $H_2Ti_4O_9{\cdot}xH_2O$ in aqueous TBAOH or an electrophoretically deposited film using exfoliated $H_2Ti_4O_9{\cdot}xH_2O$ in propylene carbonate was thermally treated at 500 °C. In these films, XRD revealed that TBA or propylene carbonate was present in the interlayer. The presence of such organic compounds in the interlayer seems to hinder the transformation of the two-dimensional structure into the three-dimensional tunnel structure, which has been proposed to be the intermediate phase.[53] The application of EPD for film processing using exfoliated $H_2Ti_4O_9{\cdot}xH_2O$ presents a significant advantage in thin film preparation of metastable oxides such as $TiO_2(B)$ since such oxides cannot be obtained by other synthetic methods (chemical vapor deposition, sol–gel, *etc.*).

Conclusions

An oriented $TiO_2(B)$ film was prepared by thermal treatment of an *a*-axis oriented $H_2Ti_4O_9{\cdot}xH_2O$ film fabricated by electrophoretic deposition using colloidal suspensions containing exfoliated $H_2Ti_4O_9{\cdot}xH_2O$. Stable colloidal suspensions containing exfoliated $H_2Ti_4O_9{\cdot}xH_2O$ were prepared by dispersing a tetrabutylammonium–$H_2Ti_4O_9{\cdot}xH_2O$ intercalation compound in various solvents. It was proposed that the positively charged tetrabutylammonium cation and negatively charged exfoliated nanosheets completely dissociate in solvents with high relative permittivity. Electrophoretic deposition of the colloidal suspensions lead to an *a*-axis oriented $H_2Ti_4O_9{\cdot}xH_2O$ film. The *a*-axis oriented $H_2Ti_4O_9{\cdot}xH_2O$ film was converted into a $TiO_2(B)$ film with the ($0k0$) planes lying perpendicular to the substrate by thermal treatment. Since bulk $TiO_2(B)$ is known to possess unique electrochemical and catalytic properties compared to other TiO_2 polymorphs, the properties of the $TiO_2(B)$ films prepared in this study are of considerable interest. Furthermore, the application of electrophoretic deposition to fabricate thin films from exfoliated oxide suspensions opens up the possibility of preparing novel metastable oxide films.



Scheme 2 Schematic showing the transformation of (left) a (200)-oriented $H_2Ti_4O_9{\cdot}xH_2O$ film to (right) a (201)-oriented $TiO_2(B)$.

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