Oversized Titania Nanosheet Crystallites Derived from Flux-Grown Layered Titanate Single Crystals

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Received May 1, 2003. Revised Manuscript Received June 27, 2003

This paper reports on the synthesis and characterization of oversized titania nanosheets derived from single crystals of a potassium lithium titanate, $K_{0.8}Ti_{1.73}Li_{0.27}O_4$. The single crystals with a lateral size of over 1 mm were obtained via a melt and recrystallization process in a flux melt. The crystals were converted into an acid-exchanged form of $H_{1.07}Ti_{1.73}O_4\cdot H_2O$, and then was reacted with aqueous tetrabutylammonium (TBA) ions at various concentrations. X-ray diffraction analysis revealed that the titanate crystals exhibited high degrees of swelling, and exfoliated single sheets were obtained at a molar TBA dose of 0.5−1 with respect to the exchangeable protons in $H_{1.07}Ti_{1.73}O_4\cdot H_2O$. Observations by transmission electron microscopy and atomic force microscopy detected very large nanosheet crystallites with a lateral size of several tens of micrometers. Some wrinkles and cracks within the crystallites indicated that they were highly flexible and also fragile.

Introduction

In the past decade, increasing attention has been paid to the delamination of a number of layered host compounds.[1] Several groups have investigated the exfoliation of functional materials such as layered titanates,[2] layered manganese oxides,[3] layered niobates,[4] and various types of layered perovskites.[5] The exfoliated single sheets can be considered as new classes of nanoscale materials, which may exhibit novel physical and chemical properties associated with their thickness of nanometer order.

Titania nanosheets are characterized by nanosized two-dimensional semiconductors. They should be interesting and useful as a relative form of a versatile material of titanium dioxide, which is attracting much attention for various applications such as photocatalysts.[6] We have studied these titania nanosheets in terms of their physicochemical properties and application to materials synthesis since we first reported the formation of nanosheets in 1996.[2a,b] Some aspects of their structural, optical, and photochemical properties have been clarified,[7] which have revealed that the titania nanosheets are distinct from the bulk form. Fabrication of various materials has been achieved by using the nanosheets as building blocks: thin flaky particulates and hollow-microspheres of TiO_2 via freeze- or spray-drying,[8] ultrathin multilayer films via electrostatic self-assembly,[2d,7c,9] and core/shell composites and hollow shells via layer-by-layer deposition on polymer bead templates.[10]

The titania nanosheets employed in these studies have been derived by delamination of a polycrystalline

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10.1021/cm034307j CCC: $25.00

sample of layered titanates.[2] The starting titanates synthesized via solid-state calcination are usually composed of platy microcrystals of ~1 μm in lateral dimension.[11] As a consequence, the resulting titania nanosheets have an average lateral size of hundreds of nanometers.[7b] Although the above-mentioned successes have been attained, submicrometer-sized nanosheets have sometimes hindered further detailed study on their physical properties such as electrical conductivity, and progress in fabrication of new materials with a well-organized nanostructure. This background has motivated us to study the swelling and delamination behaviors of single crystals of the layered titanate, by which oversized nanosheet crystallites are expected to be obtained. The situation is similar for other nanosheet materials in that their lateral size is in a range of submicro- to micrometers. Most recently, Miyamoto et al.[12] have reported the synthesis of large niobate nanosheets by delaminating precursor crystals of $K_4Nb_6O_{17}$.

Experimental Section

Materials. Titanium dioxide (rutile form), alkali metal carbonates, and molybdenum oxide of 99.9% purity or higher were used as received from Rare Metallic, Co. for the synthesis of layered titanate crystals. Other reagents were of analytical grade. Milli-Q filtered water (Millipore Co., >18 MΩ cm) was used throughout the experiments.

Flux Growth of Single Crystals of a Potassium Lithium Titanate and Their Conversion into a Protonic Form. Reagents such as TiO_2, K_2CO_3, Li_2CO_3, and MoO_3 were weighed in a molar ratio of 1.73:1.67:0.13:1.27 and mixed with intimate grinding. The mixture (100 g) was placed in a Pt crucible and reacted at 1473 K. After keeping this temperature for 10 h, the mixture was gradually cooled at a speed of 4 K h^{-1}. The sample was cooled spontaneously when the temperature reached 1223 K. The titanate crystals of $K_{0.8}[Ti_{1.73}Li_{0.27}]O_4$ were recovered by dissolving a K_2MoO_4 flux melt with water.

The obtained crystals were converted into a protonic form by applying a previously reported procedure for polycrystalline $K_{0.8}[Ti_{1.73}Li_{0.27}]O_4$.[11b] The sample (30 g) was stirred in a 0.5 mol dm^{-3} HCl solution (2 dm^3) at room temperature. The acid solution was replaced daily with a fresh one by decantation. After treatment for 5 days, the acid-exchanged crystals, $H_{1.07}Ti_{1.73}O_4{\cdot}H_2O$, were collected by filtration, washed with a copious quantity of pure water, and air dried.

Delamination. Exfoliation of the protonic titanate crystals, $H_{1.07}Ti_{1.73}O_4{\cdot}H_2O$, was attempted by reaction with a tetrabutylammonium hydroxide solution ($(C_4H_9)_4NOH$; hereafter TBAOH); 0.4 g of the protonic titanate was immersed in 100 cm^3 of the TBAOH solution.[2b,c] Its concentration ranged from 0.0025 to 0.64 mol dm^{-3}, which corresponds to a molar ratio of 0.1−25 with respect to exchangeable protons in the titanate.

Characterization. Metal contents of titanates were analyzed by ICP spectrophotometry (Seiko Instruments Inc., SPS1700HVR) after dissolving a weighed amount of sample with a mixed acid of H_2SO_4 + HF. Water content was determined from weight loss upon heating at 1273 K for 1 h.

X-ray diffraction (XRD) patterns were collected using a Rigaku Rint-2000S powder diffractometer with graphite-monochromatized Cu Kα radiation ($\lambda = 0.15405$ nm). In measurements where the wet state of the sample needed to be examined, relative humidity in the sample chamber was kept at 95% to suppress drying.

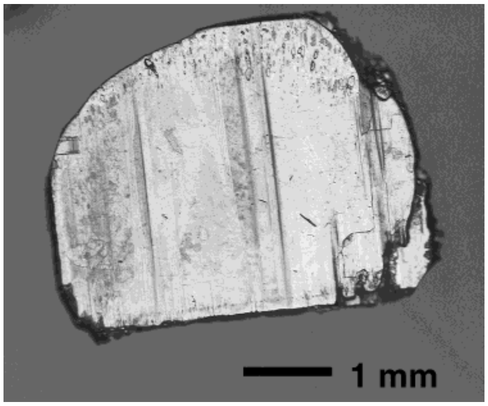

Figure 1. Single crystal of potassium lithium titanate.

Transmission electron micrographs (TEM) were obtained using a JEOL JEM-1010 electron microscope operated at an accelerating voltage of 100 kV. A TEM specimen was prepared by placing a drop of the diluted colloidal suspension ($TBA^+/H^+ = 1$) onto a holey carbon grid and removing it by soft vibration after 1 min.

Atomic force microscopy (AFM) images were recorded using a Seiko Instruments SPI-400 equipped with a wide-range scanner, which allowed us to monitor a wide area of ~150 μm. Observations were carried out in tapping mode with silicon cantilever (force constant = 40 N m^{-1}). A specimen was prepared by adsorbing titania nanosheets on a cationic surface of Si wafer coated with a monolayer of polydiallyldimethylammonium (PDDA) chloride. Monolayer formation of the nanosheets can be achieved through electrostatic self-assembly as described elsewhere[9b] by dipping the substrate into the titanate suspension (6.9×10^{-3} g dm^{-3}, pH = 11) for 20 min followed by washing it with water.

Results and Discussion

Synthesis of the Starting Titanate Crystals. Single crystals of a potassium lithium titanate were grown via a melt and recrystallization process in molten K_2MoO_4. Platy single crystals with an average lateral dimension of 4 mm were produced, as visualized by optical microscope image (Figure 1). The lateral size was larger than that of ~100 μm previously reported.[13] Initiating cooling process from a temperature higher than the melting point (~1453 K) of the titanate was found to be important to grow millimeter-sized single crystals. On the basis of XRD data (Figure 2a), the product can be identified as a potassium lithium titanate, $K_{0.8}[Ti_{1.73}Li_{0.27}]O_4$, except for a trace amount of hexatitanate ($K_2Ti_6O_{13}$) and spinel ($Li_{1.33}Ti_{1.67}O_4$). Refinement of unit cell dimensions confirmed a layered structure of lepidocrocite-type with *C*-base-centered orthorhombic cell parameters, $a = 0.3821(2)$ nm, $b = 1.5546(7)$ nm, $c = 0.2974(2)$ nm, which agrees well with the literature data.[11b]

Chemical analysis (Table 1) revealed that almost all of the constituent alkali metal ions were extracted by acid leaching for 5 days, yielding a protonic titanate. A minor residual K may be ascribed to the presence of a trace amount of $K_2Ti_6O_{13}$, because K ions in this phase cannot be extracted, as they are confined in a tunnel structure.

XRD data indicated that the layer structure was preserved with an interlayer expansion from 0.78 to 0.92

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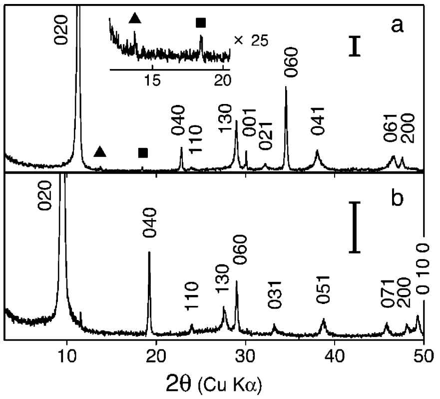

Figure 2. Powder XRD data for the potassium lithium titanate crystals (a) and acid-exchanged titanate (b). The inset profile in (a) shows two minor byproducts, corresponding to hexatitanate ($K_2Ti_6O_{13}$) and spinel ($Li_{1.33}Ti_{1.67}O_{13}$), designated by the triangle and square, respectively. Scale bar represents 200 cps.

Table 1. Chemical Analysis Data for Potassium Lithium Titanate Single Crystal and Its Acid-Exchanged Form[a]

	K_2O	Li_2O	TiO_2	Ig loss[b]	total
potassium lithium titanate single crystal					
obs.	20.0	2.1	76.1		98.2
calcd. for $K_{0.8}[Ti_{1.73}Li_{0.27}]O_4$	20.9	2.2	76.9	0.0	100.0
acid-exchanged titanate					
obs.	0.2	0.0	82.6	17.2	100.0
calcd. for $H_{1.07}Ti_{1.73}O_4{\cdot}H_2O$	0.0	0.0	83.3	16.7	100.0

[a] Values are in weight percent. [b] Weight loss at 1273 K.

nm (Figure 2b).[14] The structural and compositional changes upon acid exchange were comparable to the data for a polycrystalline sample of $K_{0.8}[Ti_{1.73}Li_{0.27}]O_4$ to $H_{1.07}Ti_{1.73}O_4{\cdot}H_2O$.[11b] The acid exchange did not bring about a significant change in morphology, but there was a reduction of crystal size to approximately half of the original (~4 mm).

Swelling and Delamination Behavior. The protonic titanate crystals of $H_{1.07}Ti_{1.73}O_4{\cdot}H_2O$ were reacted with an aqueous TBAOH solution under a range of conditions with the molar TBA dose of 0.1−25 with respect to the exchangeable protons in the titanate. The mixture was not shaken continuously to avoid the lateral fracture of the crystals due to mechanical shear, but the mixture was gently agitated by two or three strokes per day. This is very different from the experimental procedures employed for the exfoliation of a powder sample of $H_{0.7}Ti_{1.825}O_4{\cdot}H_2O$ in which vigorous shaking was applied.[2] By reaction for 2 weeks, the mixtures became turbid suspensions except for the sample at $TBA^+/H^+ = 0.1$, which was separated into solid and solution. The colloidal suspensions showed an opalescent color with a bluish tint, which was similar to those derived from a powder sample of $H_{0.7}Ti_{1.825}O_4{\cdot}H_2O$.

To obtain information on the degree of swelling, the suspensions were centrifuged at a speed of 10 000 rpm and the obtained pasty colloids were subjected to XRD measurement at a relative humidity of 95%, avoiding drying. The sample at $TBA^+/H^+ = 25$ exhibited a sharp basal diffraction series, indicating the interlayer spacing of 3.5 nm (see Figure 3). This high degree of interlayer expansion can be ascribed to “osmotic swelling”, which has been observed for smectite clay minerals,[15] layered titanate,[2b,2c] and manganese oxide[3c] in polycrystalline form. As the TBA concentration was decreased, the interlayer distance became larger and exceeded 10 nm at $TBA^+/H^+ = 2$ and below. Along with this, the basal reflections attributable to osmotic swelling declined and a broad halo pattern evolved. This broad component was predominant at $TBA^+/H^+ = 0.5{-}1$. This broad profile can be taken as evidence for complete delamination, as has been discussed in our previous paper[2b,c]; the profile showed a close match to the square of the layer structure factor calculated based on the structure of the host layer in $H_{1.07}Ti_{1.73}O_4{\cdot}H_2O$ (a dotted trace in Figure 3f).[16] At the lowest TBA dose of $TBA^+/H^+ = 0.1$, there was not the broad component but two different basal diffraction series, indicating the presence of two phases with the interlayer distance of 0.92 and 1.62 nm. These were identified as the unreacted protonic titanate and a TBA intercalated material, respectively.

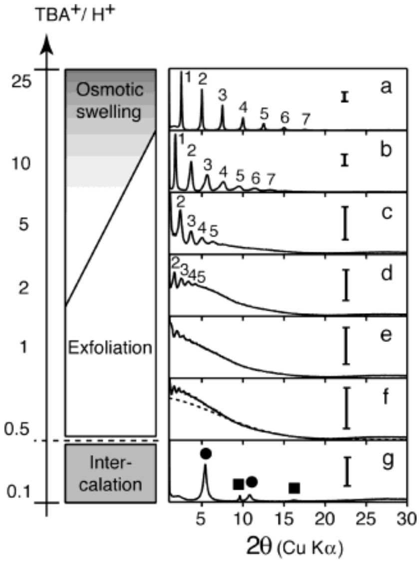

Figure 3. XRD patterns for a colloidal aggregate centrifuged from suspensions with various TBA contents. The molar ratio of TBA ions over exchangeable protons in the titanate, TBA^+/H^+, is 25 for (a), 10 for (b), 5 for (c), 2 for (d), 1 for (e), 0.5 for (f), and 0.1 for (g). The interlayer spacing from basal diffraction series in (a) − (d) are 3.5 nm, 4.8 nm, 7.4 nm, and 10.2 nm, respectively. Two sets of diffraction series in (g), designated by circles and squares, have basal spacings of 1.63 and 0.92 nm. Digits next to the lines represent the order of basal diffraction series. Scale bar represents 5000 cps. A dotted plot in (f) represents the square of structure factor calculated based on the single layer in $H_{1.07}Ti_{1.73}O_4{\cdot}H_2O$.

On the basis of the XRD data above, the reaction diagram of the layered titanate single crystals and aqueous TBAOH can be summarized as shown in Figure 3. XRD analysis of the colloids indicated that large

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[14] Unit cell dimensions: $a = 0.3781(1)$ nm, $b = 1.8452(9)$ nm, $c = 0.2989(2)$ nm.

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[16] The structure factor was calculated as $F(\theta) = 0.865\, f_{Ti} \exp 2\pi i (y_{Ti}{\cdot}\sin\theta/\lambda) + f_O \exp 2\pi i (y_{O1}{\cdot}\sin\theta/\lambda) + f_O \exp 2\pi i (y_{O2}{\cdot}\sin\theta/\lambda)$, where f_{Ti}, f_O are atomic scattering factors for Ti and O, and λ is the X-ray wavelength. Atomic locations are $y_{Ti} = \pm 0.075$ nm, $y_{O1} = \pm 0.225$ nm, and $y_{O2} = \pm 0.075$ nm, which are based on the ideal layer architecture of lepidocrocite-type. For a detailed description, see ref 2c.

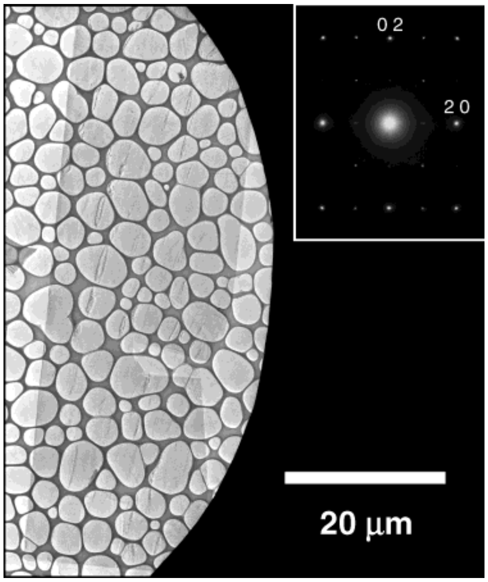

Figure 4. TEM image of oversized titania nanosheet. The insert shows the selected area electron diffraction pattern.

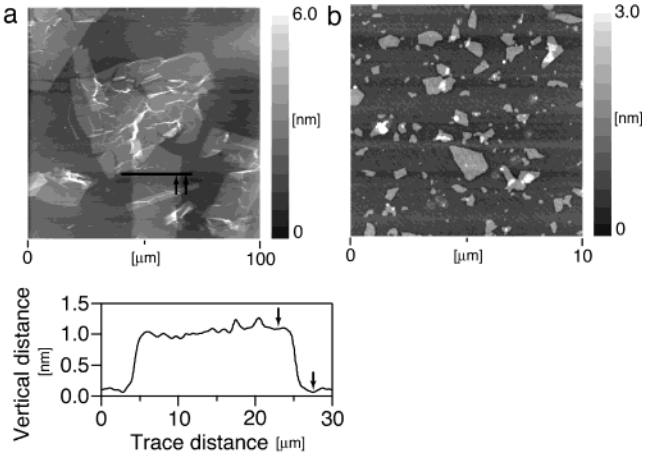

Figure 5. AFM image of nanosheets obtained by delamination of titanate crystals by (a) agitation by a couple of strokes per day and (b) continuous shaking at 170 rpm.

single crystals of the layered titanate undergo high degrees of swelling and exfoliation reactions upon interaction with aqueous quaternary ammonium ions, the process of which is basically similar to that for the powder sample of microcrystals, $H_{0.7}Ti_{1.825}O_4{\cdot}H_2O$.[2c] One noticeable difference is the narrower and relatively lower range of TBA^+/H^+ where complete delamination took place. A higher layer charge of $H_{1.07}Ti_{1.73}O_4{\cdot}H_2O$ may be responsible for this difference. It is important to note that the “total” delamination of large single crystals to single sheets was clearly demonstrated by XRD data. This is different from evidence based on microscopy data, which sometimes does not reveal a major feature.

Characterization of Exfoliated Sheets. The sample at $TBA^+/H^+ = 1$ was examined by TEM and AFM observations to characterize the morphology of the exfoliated material. In TEM images, thin crystallites showing very faint contrast were observed, as visualized by a typical image in Figure 4. The crystallites had sharp edges, reflecting the morphology of the parent crystals. Their lateral size showed some distribution ranging from 10 μm to 100 μm with a most frequent value of ~30 μm. This is much larger than the nanosheets derived from a powder sample synthesized via solid-state calcinations,[7b] which were mostly in a range of 100−500 nm. The faint and uniform contrast within one crystallite implies its extremely small thickness. Furthermore, its single-crystal nature was confirmed by selected area electron diffraction exhibiting a spot pattern (see the inset of Figure 4). The rectangular lattice with $a = 0.38$ nm and $c = 0.30$ nm is compatible with the two-dimensional atomic arrangement of lepidocrocite type, indicating that the basic layer architecture remained unchanged after exfoliation. However, the pattern showed additional spots with indices of $h + l = 2n+1$ that are not allowed for the faced-centered arrangement of the titanate sheet on the projection along its sheet normal. The existence of these spots may be accounted for by a minor structural modification induced by delamination or Warren effect (i.e., diffuse rod along the k axis). A conclusion should await further study.

AFM observations also demonstrated the formation of oversized nanosheets (Figure 5). The crystallites with lateral dimensions of tens of micrometers comparable to that in the TEM image were found at the substrate surface. The height profile revealed that the nanosheets had a fairly flat terrace having a thickness of ~1.0 nm. This value is similar to the ~1.2 nm observed for the small nanosheets derived from polycrystalline titanate, which has been explained by the nanosheet with an adsorbed monolayer of water molecules on both its surfaces.[7b] The lateral size was comparable to that for niobate nanosheets prepared from millimeter-sized $K_4Nb_6O_{17}$ crystals. The niobate sheets are of bilayers while the oversized nanosheets are unilamellar.

Another noteworthy feature is high flexibility. The nanosheets adsorbed on the substrate look like a very thin cloth having a number of wrinkles. This highly flexible nature may be a good index for the nanosheet crystallite that can be classified as an inorganic macromolecule. The lateral size of the nanosheets was less than 100 μm, although the protonic titanate crystals before delamination had an average size of several millimeters. This suggests that the exfoliation reaction with aqueous TBA ions accompanied the lateral fracture to some extent, despite our careful efforts. We attempted to delaminate the titanate crystals without extensive mechanical shear. TEM and AFM images showed cracks in the crystallites. This suggests that the nanosheets are cleaved fairly easily. The extremely small thickness of ~1 nm is apparently responsible for this. Figure 5b shows the AFM image for a nanosheet sample obtained in a control test where the delamination was carried out by continuous shaking at 170 rpm for 2 weeks. Drastic reduction in lateral size to the micrometer range is evident.

Conclusions

We have demonstrated the formation of oversized titania nanosheets with a lateral size of several tens of micrometers and a thickness of ~1 nm. The obtained crystallites are approximately 10 000 times larger in area than those of the titania nanosheets synthesized so far. We expect that exploration of the inherent physical properties may be facilitated with these oversized nanosheets. Furthermore, it will be of interest to employ these crystallites in the fabrication of some nanostructured materials.

Acknowledgment. This work has been supported by CREST of JST (Japan Science and Technology Corporation). We are grateful to Mr. Satoshi Takenouchi of our Institute for his assistance in the chemical analysis of potassium lithium titanate single crystals and its acid-exchanged form.

CM034307J