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Macromolecular Nanoplatelet of Aurivillius-type Layered Perovskite Oxide, $Bi_4Ti_3O_{12}$

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The molecular architecture of inorganic−inorganic/inorganic−organic heterostructured nanohybrids is of great interest because it provides a means of creating new nanohybrid materials with enhanced physicochemical functions. Such molecular manipulation has been achieved by various techniques such as layer-by-layer (LBL) assembly,[1] the Langmuir−Blodgett technique,[2] and the intercalation reaction.[3] Because the exfoliated individual nanosheet can be considered as a nanoparticle or an inorganic supramolecule, which is a basic building block for heterostructured nanohybrids, the exfoliation and restacking processes of 2-D inorganic materials such as clays, zirconium phosphate, metal chalcogenides, and metal oxides such as titanate and titanoniobate have been intensively studied.[4a−e] In this work, we attempted to exfoliate the layered perovskite oxides, $Bi_4Ti_3O_{12}$ (BTO), into individual nanoplatelets with the thickness of a few nanometers (Figure 1). Recently, Aurivillius-type layered perovskite oxides such as $Bi_4Ti_3O_{12}$ (BTO), $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT), and $SrBi_2Ta_2O_9$ (SBT) have attracted much attention due to their fatigue-free behaviors in a nonvolatile ferroelectric random access memory (NVFRAM) device.[5] In the present study, we were able to prepare a translucent colloidal suspension of BTO nanoplatelets for the first time, which can be applied to electronic nanodevices as ultrathin insulators or dielectrics.[6]

The starting BTO material was prepared by a conventional solid-state reaction. A stoichiometric amount of Bi_2O_3 and TiO_2 was mixed, pelleted, and then fired at 1000 °C in an electric furnace to prepare the pristine BTO. By reaction of the BTO powder with 3-mol excess of *n*-BuLi in hexane for at least 3 days, the lithiated BTO (LiBTO) could be obtained. The resulting black powder was washed with hexane more than five times and then dried in vacuo. The exfoliated product was obtained as a suspension when deionized water was added to the LiBTO powder, and it was collected by centrifugation at 13 000 rpm for 60 min and then washed with deionized water several times to remove LiOH until the pH of the supernatant became 7. The washed product was redispersed in water to form a translucent suspension after it was subjected to ultrasonic irradiation in an ultrasound bath for about 1 h. When the BTO suspension was intermixed with an aqueous solution of cetyltrimethylammonium bromide surfactant ($CTA^+Br^-/\sim 10^{-3}$ M)/poly(acrylic acid) (PAA/M.W. ∼ 2000/0.1 wt %), a clear suspension of BTO with a slightly cyanic color could be obtained.[7]

When the *n*-BuLi is added to BTO bulk powder, the color of the resulting product ($Li_2Bi_4Ti_3O_{12}$; LiBTO) immediately changes from yellowish white to black due to a partial reduction of bismuth and titanium.[8] According to a neutron diffraction study,[8] it has been found that the Li^+ ion is positioned between the apex oxygens of the $Bi_2Ti_3O_{10}{}^{2-}$ perovskite blocks and the square planar oxygens of the $Bi_2O_2{}^{2+}$ layer. The exfoliated BTO nanoplatelets were obtained as a suspension when deionized water was added to the Li-intercalated BTO (LiBTO) powder. The exfoliation reaction of LiBTO seems to be similar to that of MS_2 (M = Mo and W); $Li_2Bi_4Ti_3O_{12} + H_2O \rightarrow Bi_4Ti_3O_{12}$ (exfoliated) $+ 2LiOH + {}^1/_2H_2$.[4c] During the reaction with H_2O, the lithium ion is extracted into solution as LiOH together with hydrogen evolution and, therefore, the gap between the perovskite blocks and the $Bi_2O_2{}^{2+}$ layer splits apart.

Figure 2 shows an atomic force microscopy (AFM) image of the exfoliated BTO single sheet deposited on silicon substrate.[9] A surface profile along the line in Figure 2 indicates that the vertical and lateral dimensions of the exfoliated BTO platelet are 1.5−1.8 and 50−100 nm, respectively (the lower panel of Figure 2). The average height is determined to be 1.6 ± 0.5 nm, which

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(7) Elemental analyses for Bi, Ti, and Li of the Li-intercalated BTO phase were performed by inductively coupled plasma (ICP) and atomic absorption (AA) spectroscopic methods. The chemical formula of the LiBTO powder was determined as $Li_{2.1(1)}Bi_{4.0}Ti_{3.1(1)}O_{12}$. The stoichiometry of restacked BTO film from the suspension was also analyzed by electron probe microanalysis (EPMA). The bismuth content was not changed after the exfoliation and restacking processes within the limit of experimental error (<10%).

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(9) BTO nanoplatelets were placed on silicon substrate by dipping in a diluted suspension ($\sim 10^{-7}$ M), and then its surface topography was examined by AFM. A nanoscope AFM and oxide-sharpened Si_3N_4 tips from digital instruments were used. The piezo scanner has a range of 10 μm. All the images were obtained with tips of a nominal spring constant of 0.12 N/m. The AFM images were obtained in the contact mode under 0.5 nN probe force and at a pixel resolution of 512 × 512.

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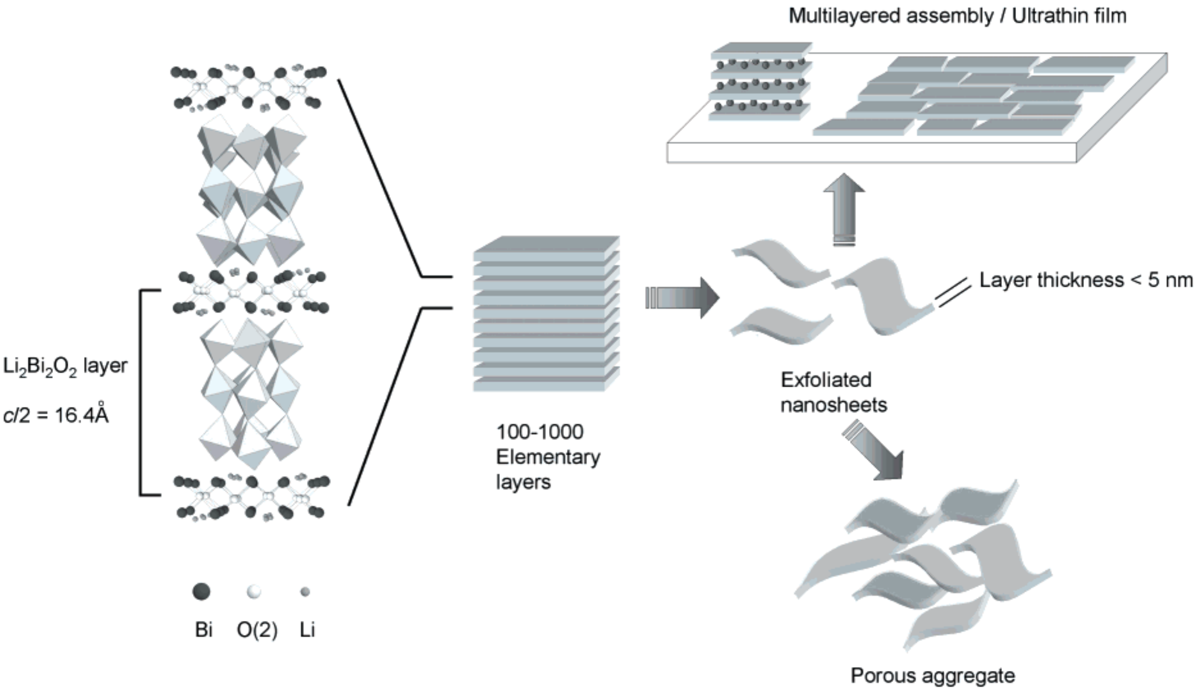
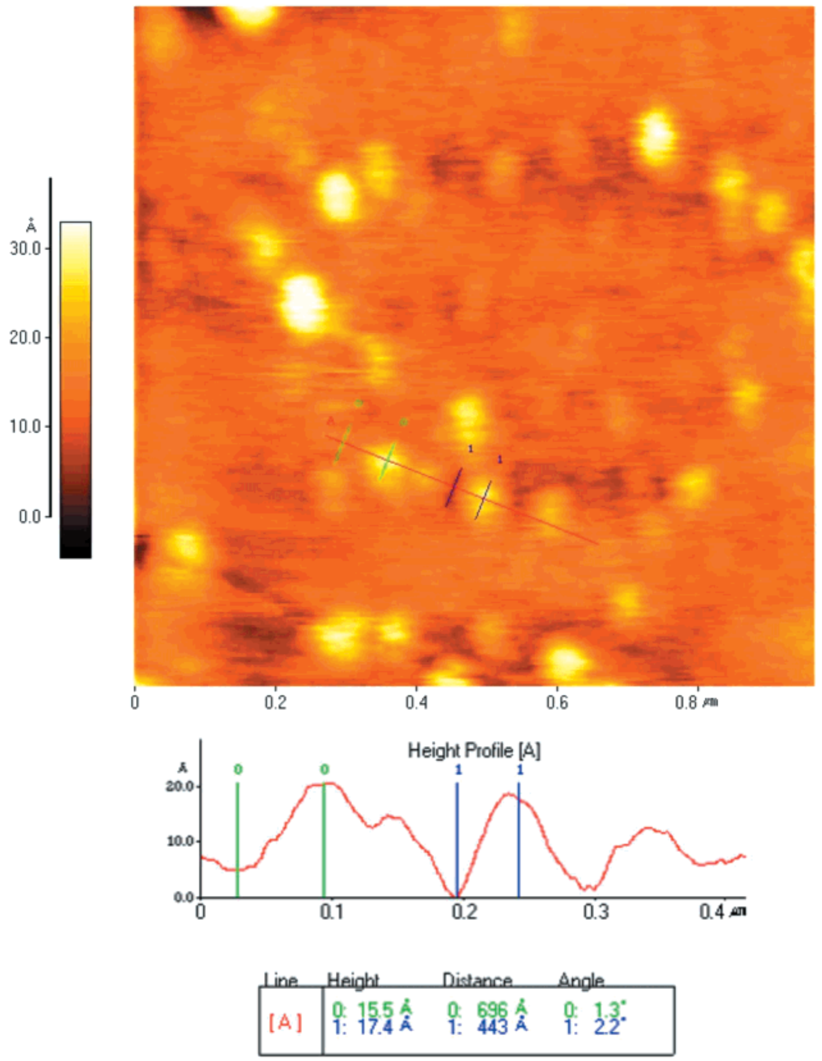


Figure 1. Schematic illustration of exfoliation and restacking process.



Line	Height	Distance	Angle
[A]	0: 15.5 Å 1: 17.4 Å	0: 696 Å 1: 443 Å	0: 1.3° 1: 2.2°

Figure 2. Upper panel: Atomic force microscopic image of BTO nanoplatelet on a silicon substrate (1 × 1 μm area). Lower panel: Height profile for the cross section along the line indicated in AFM image.

is very close to half the *c*-axis lattice parameter ($c/2 = 16.4$ Å) corresponding to the exfoliated BTO single layer.

Figure 3 shows high-resolution transmission electron microscopy (HRTEM) images for the cross-sectional view of the exfoliated BTO nanoplatelet.[10] The suspension of BTO nanoplatelets in an aqueous PAA solution was embedded in resin, sliced by an ultramicrotome, and then examined by HRTEM. The BTO layers consist of equally spaced parallel lattice fringes, which appear with dark contrast in the TEM images. Regularly spaced parallel layers (lattice fringes) represent the heavy atoms of bismuth. As indicated in Figure 3a, exfoliated thin flakes having a thickness of a few nanometers are stacked randomly without any particular structure. However, the cross-sectional views provide unambiguous evidence for the exfoliation into the nanoplatelet consisting of several repeating units of the BTO structure. Figure 3b shows that the submicron-sized BTO crystal was exfoliated into thin flakes having a thickness of <5 nm. Because one repeating unit in the crystal structure of BTO is ~16 Å ($c/2$), the layer thickness of approximately 5 nm corresponds to three repeating units, i.e., 3×16 Å $= 48$ Å. As shown in Figure 3c, the folded thin flakes are also observed in the magnified view of a smaller region (indicated by arrows in Figure 3b).

In conclusion, the exfoliated BTO nanoplatelets were obtained as suspensions when the Li intercalate was reacted with H_2O. From atomic force microscopy (AFM) and high-resolution transmission electron microscopy (HRTEM) images, we were able to confirm that the submicron-sized BTO particles were exfoliated into elementary nanosheets having a layer thickness of ≤5 nm. Since bismuth titanate, which is well-known as a ferroelectric material,[5] can be also used as an electrical insulator,[6] diffusional barrier,[11] mediator for electron transfer,[1a] etc., multilayered assemblies including other organic/inorganic species with specific function may provide interesting and versatile physicochemical characteristics.

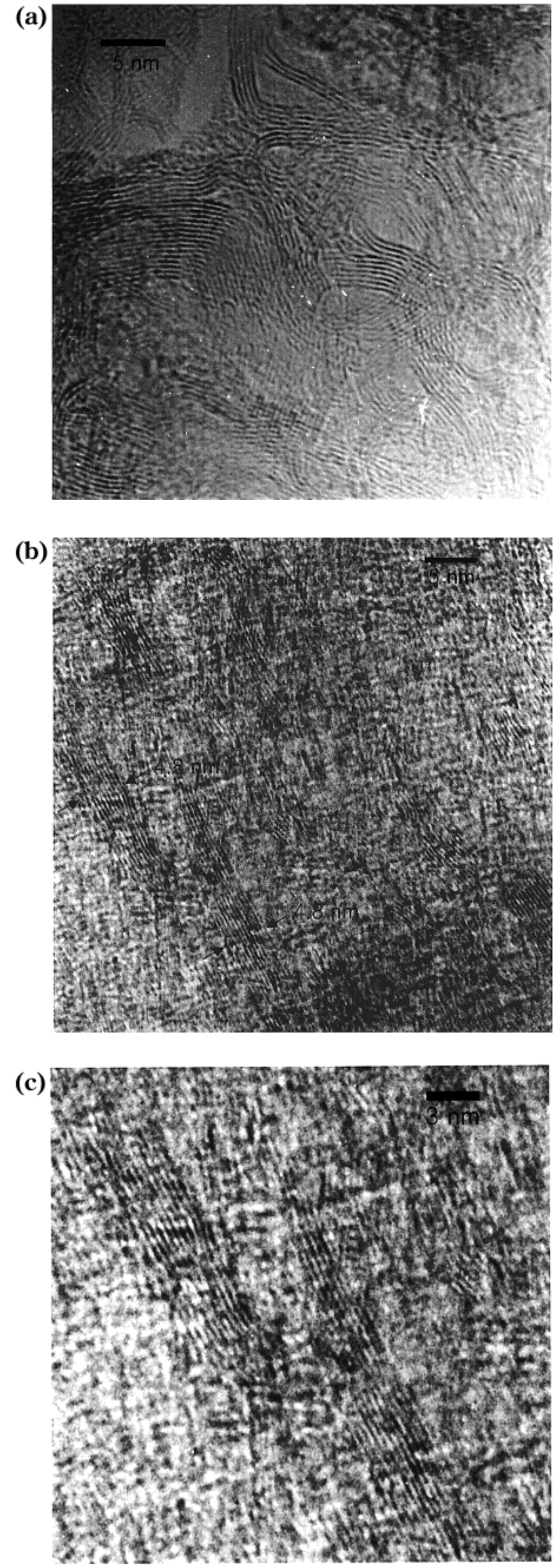


Figure 3. (a) Cross-sectional HRTEM image of the exfoliated BTO nanoplatelets. The exfoliated nanosheets are coagulated in acrylic resin matrix. (b) HRTEM image showing the exfoliated BTO nanosheets. As indicated by arrows, the layer thickness of thin flakes is approximately 4.8 nm, which corresponds to three repeating units. (c) The magnified view of the region indicated by arrows in (b).

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Supporting Information Available: Experimental data; tables of atomic positions and isotropic temperature factors and selected bond distances; and figures of the crystal structures of $Bi_4Ti_3O_{12}$ and $Li_2Bi_4Ti_3O_{12}$, the neutron diffraction profiles for $Li_2Bi_4Ti_3O_{12}$, the difference Fourier map for $z = 0.313$ showing the location of Li atoms, and FE-SEM micrographs of the as-deposited BTO thin film (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[10] The suspension of BTO in an aqueous solution of 0.1% poly(acrylic acid) was dried on a slide glass. The *ab* plane of the BTO platelet was oriented parallel to the substrate and then embedded with acrylic resin (methyl methacrylate:*n*-butyl methacrylate = 4:6, benzoyl peroxide 1.5%) in a polyethylene capsule. The embedded samples were cut by a diamond knife in an ultramicrotome and produced into thin specimens for high-resolution transmission electron microscopy (HRTEM) study. The slicing speed and thickness were set to 1.2 mm/s and 50 nm, respectively. The thin sections were then located onto a microgrid covered with a carbon thin film. Electron microscope observations were carried out with a Hitachi H-9000NA TEM at an accelerating voltage of 300 kV.

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