Electronic Supplementary Information (ESI)

Few-layered titanate nanosheets with large lateral size and surface functionalization: Potentials for controlled exfoliation of inorganic-organic layered composite

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Experimental methods

All the reagents were used as purchased without purification.

Synthesis of the layered (R-BA)-TiO_2 and its exfoliation: The (R-BA)-TiO_2 was synthesized through the ion exchange of the precursor layered H-TiO_2. The layered H-TiO_2 was synthesized from Cs-TiO_2 by the method reported in previous works.[9,14] The H-TiO_2, typically 0.2 g, was immersed in an aqueous solution containing benzylamine (R-BA), such as 4-aminobenzylamine (NH_2-BA, TCI, 98.0%), 4-(aminomethyl)phenol (OH-BA, TCI, 98.0%), 4-fluorobenzylamine (F-BA, TCI, 98.0%), and 4-methylbenzylamine (CH_3-BA, TCI, 98.0%) for 10 days at 25 °C under stirring. The molar ratio of the interlayer proton to R-BA was set at 1.0. The resultant (R-BA)-TiO_2 powder was washed with purified water and ethanol and then dried. For the exfoliation, 50 mg of the (R-BA)-TiO_2 powder was dispersed in 20 cm^3 of acetonitrile (Kanto, 99.5%). The dispersion liquid was maintained at 60 °C for 5 days under stirring. The bulk precipitate was removed by centrifugation at 9000 rpm for 15 min. The resultant dispersion liquid was used for the characterization.

Characterization: The crystal structure and the interlayer distance were analyzed by X-ray diffraction (XRD, Rigaku Mini Flex II and Bruker D8 Advance) with Cu-Kα radiation. The contents of organic molecules in the layered composites were estimated by thermogravimetry (TG) analysis (Seiko, TG-DTA 7000) in air atmosphere. The detailed process for calculation of the chemical composition was described in Fig. S1 in the ESI. The morphologies of the layered composites were observed by field-emission scanning electron microscopy (FESEM, FEI Sirion, Hitachi S-4700, and JEOL JSM-7600F) operated at 5.0 kV. The lateral size and the thickness of the exfoliated sheets were measured on the images of atomic force microscopy (AFM Shimadzu, SPM-9700). The dispersion liquid of the nanosheets was dropped on a cleaned silicon substrate heated at 100 ˚C by using a temperature-controlled stage. The nanosheets were also observed by field-emission transmission electron microscopy (FETEM, FEI, Tecnai F20) operated at 200 kV. The dispersion liquid was dropped on a collodion membrane with copper grid. The UV-Vis absorption spectra of the solid-state layered composites were obtained by a spectrophotometer (Jasco, V-670) with an integrated sphere. The spectra of the dispersion liquid and the solution were measured in a quartz glass cell by a transmittance mode. The valence of titanium in the (NH_2-BA)-TiO_2, H-TiO_2, and commercial anatase TiO_2 (Kanto, Titanium (IV) oxide anatase form, 98.5 %) was analyzed by X-ray photoelectron spectroscopy (XPS, JEOL, JPS-9010TR).

XRD patterns and TG curves of the (R-BA)-TiO_2

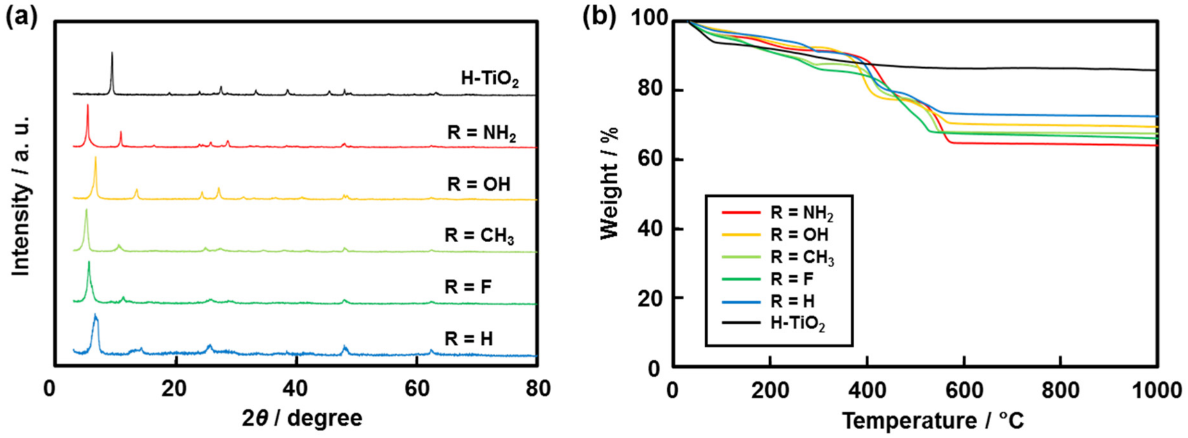

Fig. S1. XRD patterns (a) and TG curves (b) of the precursor (R-BA)-TiO_2.

The interlayer distance (d_0) in Table 1 was calculated from the XRD pattern (Fig. S1a). The composition of the (R-BA)-TiO_2 was estimated from the weight loss on the TG curves as the following procedure (Fig. S1b). According to a previous report, the composition of the H-TiO_2 is assumed to be $H_{0.7}Ti_{1.825}\square_{0.175}O_4\cdot yH_2O$ ($\square$: vacancy).[14] Since the interlayer proton is exchanged to R-BA^+, the chemical formula is assumed to be $(R\text{-}BA^+)_xH_{0.7-x}Ti_{1.825}\square_{0.175}O_4\cdot yH_2O$ after the intercalation of R-BA. The content of water (y) and R-BA^+ (x) (Molecular weight: $M_{R\text{-}BA+}$) was estimated from the weight losses below 140 °C and in the range of 140–600 °C, respectively (Fig. S1b). The final product after the heating at 1000 °C is assumed to be $Ti_{1.825}\square_{0.175}O_4$ (Formula weight: F_{TiO2} = 151.36 g mol^{-1}). If the weight of R-BA^+ and $Ti_{1.825}\square_{0.175}O_4$ on the TG curve is respectively $W_{R\text{-}BA+}$ and W_{TiO2}, the content of R-BA^+ (x) can be calculated by the following equation: $W_{R\text{-}BA+} : W_{TiO2} = x\cdot M_{R\text{-}BA+} : F_{TiO2}$. The calculated x was listed in Table 1.

The tilted angle of the intercalated molecules was estimated from the d_0 and the molecular length. The molecular length was calculated to be 0.61 nm for NH_2-BA, 0.62 nm for OH-BA, 0.64 nm for CH_3-BA, 0.49 nm for H-BA, and 0.62 nm for F-BA. The tilted angle was estimated to be around 50° for CH_3-BA and 30° for OH-BA on the assumption that the intercalated molecules form the tilted bilayer structure.

Photographs and UV-Vis spectra of the (R-BA)-TiO_2

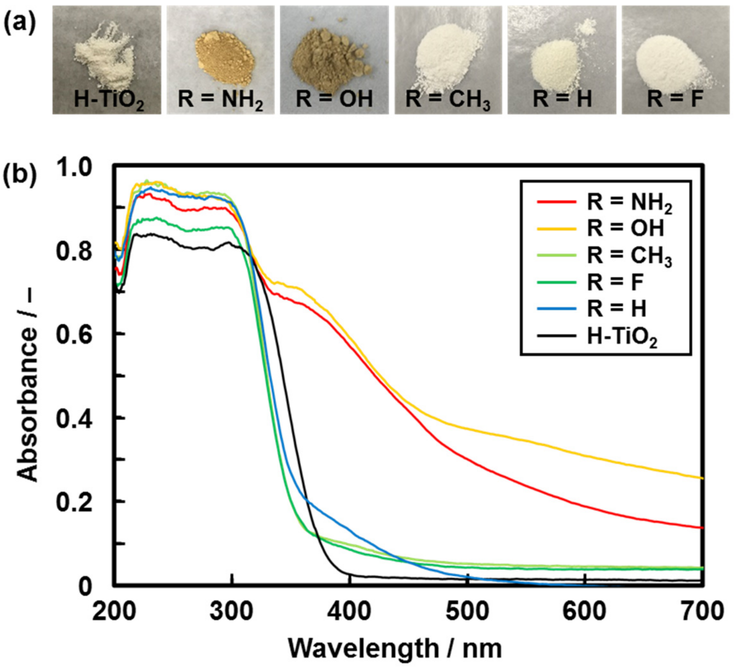

Fig. S2. Photographs (a) and UV-Vis spectra (b) of the precursor (R-BA)-TiO_2.

Whereas the color of H-TiO_2 powder was white (Fig. S2a), the (R-BA)-TiO_2 (R = NH_2 and OH) samples showed brown with absorption in visible-light region longer than 400 nm (Fig. S2b). In contrast, the color of the (R-BA)-TiO_2 (R = CH_3, H, and F) samples was not so changed after the intercalation of the R-BA. Table 1 summarizes the absorbance at 400 nm. The absorbance and absorption spectrum were changed by the R of the R-BA. The electron withdrawing and donating natures of the R have effects on the absorption properties.

XPS analysis of the (NH_2-BA)-TiO_2 and the reference samples

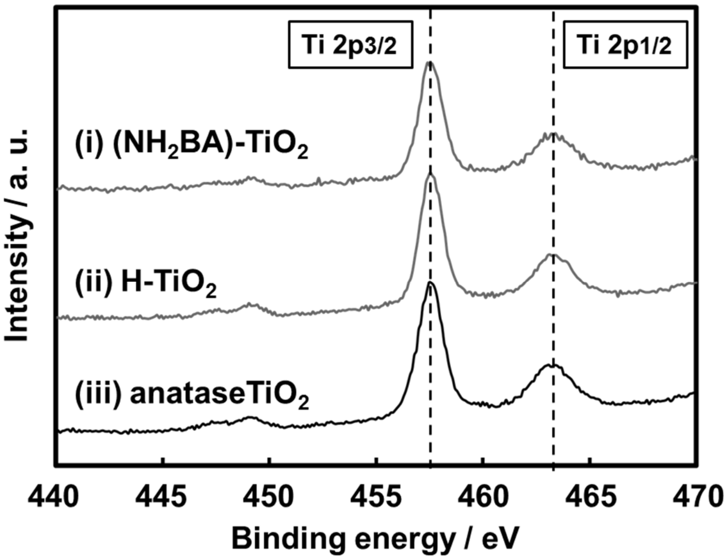

Fig. S3. XPS data of the (NH_2-BA)-TiO_2 (i), H-TiO_2 as the starting material (ii), and commercial anatase TiO_2 as the reference (iii).

The presence of Ti^{3+} in titanium oxide shows the shoulders in the lower binding-energy region on the Ti2$p_{3/2}$ and Ti2$p_{1/2}$ peaks of the Ti^{4+},[15] although the values of the binding energy, namely the peak positions, are slightly different in the reports. No such spectroscopic changes were observed on the (NH_2-BA)-TiO_2 samples after the intercalation of the NH_2-BA compared with the starting H-TiO_2 and commercial anatase TiO_2 (Fig. S3). The results indicate that Ti^{3+} was not generated in the (NH_2-BA)-TiO_2. Therefore, the color change is ascribed to not the formation of Ti^{3+} but the charge transfer excitation from the HOMO of NH_2-BA to the CB of the titanate layer in the present work.

TEM and AFM images of the (NH_2-BA)-TiO_2 nanosheets

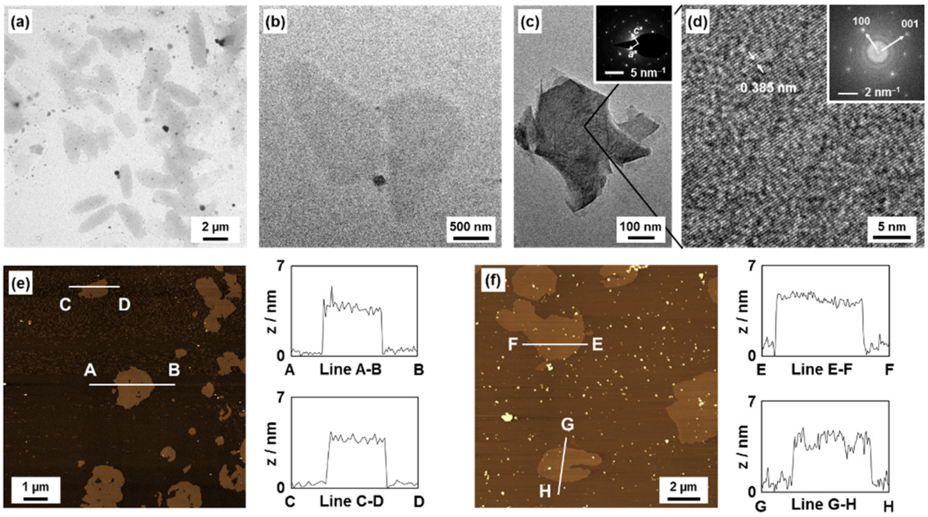

Fig. S4. TEM (a–d) and AFM (e,f) images of the (NH_2-BA)-TiO_2 nanosheets dispersed in acetonitrile. (a,b) TEM images of the few layers. (c) TEM images of the stacked thicker nanosheets with the SAED pattern (the inset). (d) The magnified images of the panel and the Fourier-transform (the inset). (e,f) Additional AFM images and their height profiles.

The nanosheets with the same lateral size were observed on the TEM images as well as the AFM images (Fig. S4a,b). The lattice fringes were observed on the stacked thicker nanosheets (Fig. S4c,d). The spot pattern and the lattice fringes corresponding to the (100) and (001) planes of titanate were observed on the SAED pattern and the Fourier transform, respectively (Fig. S4c,d).[14] On the basis of the AFM images, the histogram of the lateral size and thickness were prepared in Fig. 3c in the main text. The yield in the main text was estimated from the weight of the collected nanosheets by using filter paper with the pore size around 100 nm.

Tauc's plot for estimation of the E_g

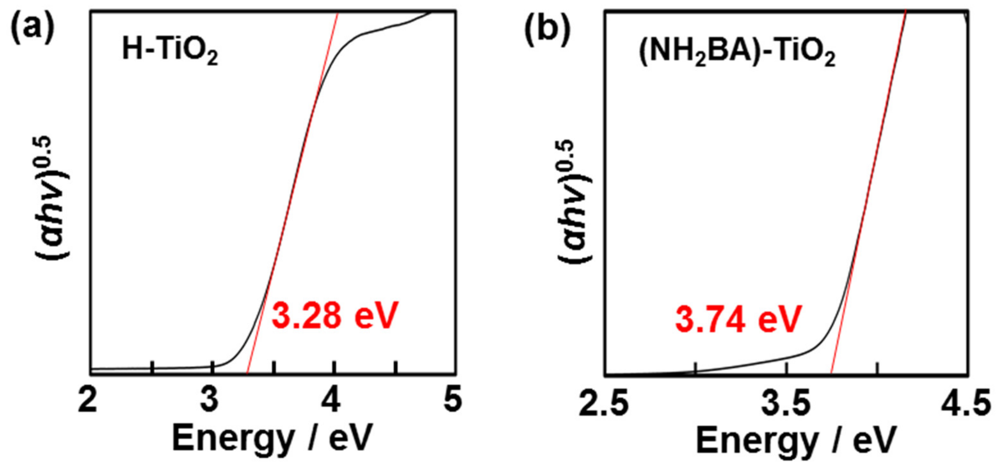

Fig. S5. Tauc's plot for estimation of the E_g of the layered H-TiO$_2$ (a) and the (NH$_2$-BA)-TiO$_2$ few layer (b).

The E_g of the titanate in the layered H-TiO$_2$ (a) and the (NH$_2$-BA)-TiO$_2$ few layer (b) was estimated from the Tauc's plots. The Tauc's plots for estimation of the $E_{g,\mathrm{HOMO\text{-}CB}}$ were displayed in the inset of Figs. 2d and 3d in the main text. The related energy level was summarized in Fig. 3e.