Supplementary Information

Mass production of Titanium Oxide ($Ti_2O_5^{2-}$) Nanosheets by a Soft, Solution Process

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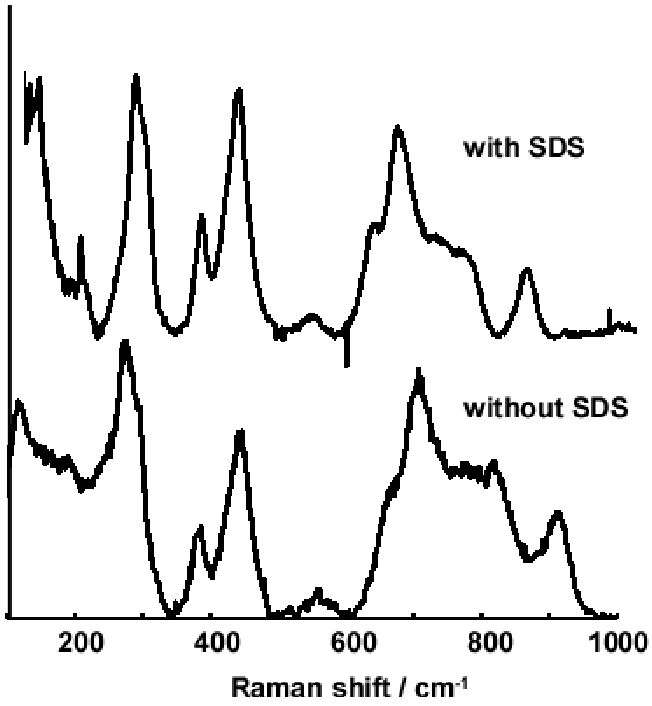

Figure S1. Raman spectra of the prepared layered titanium oxides. These spectra are in agreement with those of $Na_{2-x}H_xTi_2O_5$•$1.8H_2O$, $K_2Ti_2O_5$, and water-treated $Cs_2Ti_2O_5$.[S1-S3]

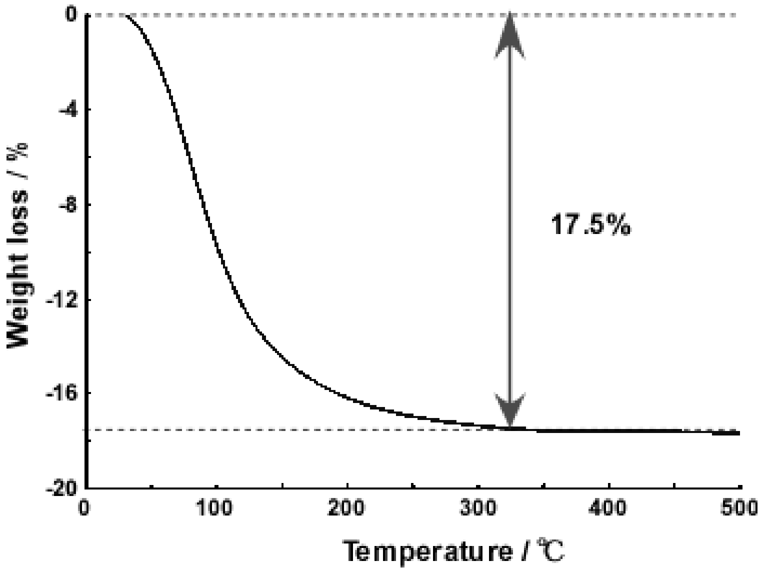

Figure S2. Thermal analysis (TG) results of the layered oxide. The mass loss of 17.5% at temperatures less than ~330 °C is due to the release of intercalated water.

Figure S3. Photograph of the mass-product DS nanosheet solution (2L, 3.9×10^{-3}M).

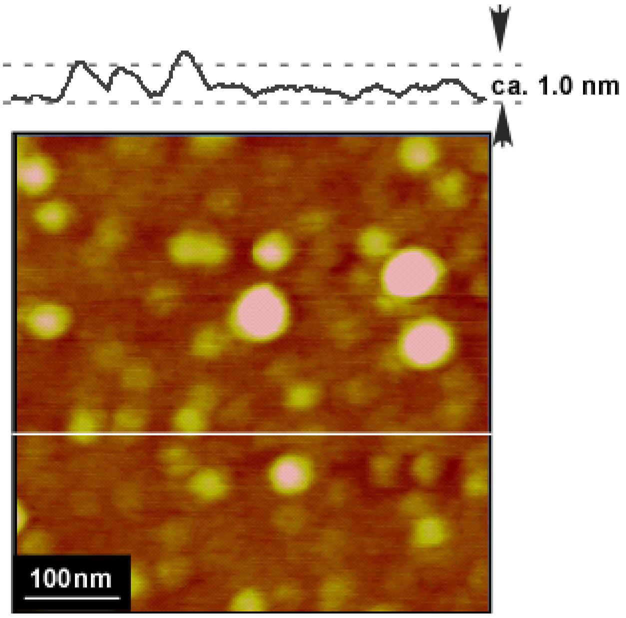

Figure S4. AFM image and depth profile of the DS nanosheets. Because of the nanosheets' small lateral sizes (few nanometers), they appear as particles (the limitation of the AFM tip with respect to lateral size is ~10–20 nm).

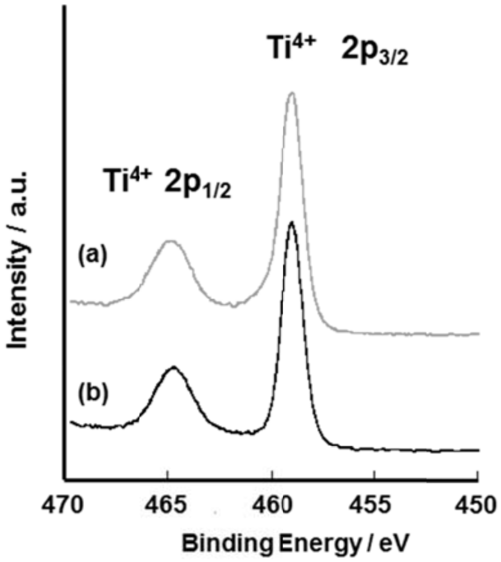

Figure S5. XPS spectra of $Ti2p_{1/2}$ and $2p_{3/2}$ for (a) layered oxide precursor and (b) nanosheets. All of Ti exist as Ti^{4+}.

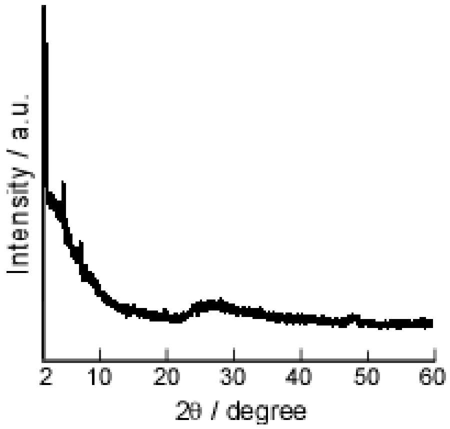

Figure S6. XRD pattern of colloidal aggregate obtained by centrifugation of the suspension at 20000rpm. The absence of sharp basal reflections suggests the collapse of the layered structure. Instead, an amorphous-like halo was detected in the low-angular region, which could be attributed to the scattering from the randomly aggregated unilamellar nanosheets.

Experimental.

We synthesized titanium oxide nanosheet precursors by mixing aqueous solutions of $(NH_4)_2[TiO(C_2O_4)_2]$, KOH, and SDS (for DS nanosheets) as follows. Solutions of $(NH_4)_2[TiO(C_2O_4)_2]$, (0.13 M), KOH (2 M), and SDS (0.13 M) were prepared with distilled water. $(NH_4)_2[TiO(C_2O_4)_2]$, (20 mL), KOH (10 mL), and SDS (20 mL) were mixed in a 100 cm^3 vessel to precipitate the nanosheet precursor and were stirred for 1 day at a temperature between room temperature and 80 ℃. After the reaction, the precipitates obtained were centrifuged (3000 rpm, 20 min), washed with distilled water and ethanol, and dried at room temperature under vacuum.

The delamination of the deposits ($K_{1.1}H_{0.9}Ti_2O_5•2.6H_2O$) was performed as follows. The powdered material ($K_{1.1}H_{0.9}Ti_2O_5•2.6H_2O$, 0.1 g) was mixed with a TBAOH aqueous solution (0.1 M, 100 mL) to delaminate the host layers under slow stirring conditions for 1 day. The suspensions were subsequently centrifuged (3000 rpm, 10 min), and the supernatants were used as nanosheet solutions.

The crystal structure was analyzed using XRD patterns (Rigaku RINT-2500VHF, equipped with a Cu Kα radiation source). The thickness of the delaminated nanosheets was confirmed by AFM (Digital Instruments Nanoscope V, tapping mode) measurements; the samples for the AFM observations were prepared by spin coating of the diluted nanosheet solution (nanosheet solution obtained by centrifugation of the suspension at 20 000rpm) onto mica substrates[S4]. The samples were dried under pure N_2 at room temperature. For TEM (Hitachi, HF-2000, 200 kV) observations, one drop of the aqueous nanosheet suspension was deposited onto a holey carbon film. XPS (Thermo Scientific, Sigma Probe) was used to analyze the layered oxides and nanosheets. A monochromatized X-ray source (Al Kα, hν = 1486.6 eV) was used for the XPS measurements. For these measurements, a Pt substrate (in nanosheet/Pt film) was used to determine the Fermi level. Raman spectroscopy was performed using a micro-Raman spectrometer (Jasco NRS-3100) with a 532 nm excitation source at room temperature. The concentration of the nanosheets in the solution was analyzed by an inductively coupled plasma spectrometer (Seiko Instruments, SPS7800), where the nanosheets were dissolved in the nanosheets were dissolved in concentrated HCl before measurements. UV–vis absorption spectra were obtained using a Jasco V-550 spectrometer. Thermogravimetric–differential thermal analysis curves for the layered oxides were obtained by thermal analysis (Seiko TG/DTA).

Photoluminescence spectra were analyzed with a Jasco FP-6500 spectrofluorometer equipped with a 150 W Xe lamp. Photoluminescence spectra of sample solutions ($Eu(NO_3)_3$, or nanosheet solutions, etc.) were prepared and placed in a square quartz cell.

References

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