Supporting Information

Colloidal unilamellar layers of tantalum oxide with open channels

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Material synthesis. RbTaO₃ with a monoclinic layered structure was synthesized as a precursor of the holey nanosheets by calcination of a mixture of Rb₂CO₃ and Ta₂O₅ (1.02:1 molar ratio) at 1173 K for 20 hours. The hygroscopic product of RbTaO₃ was reacted with a 1 mol dm⁻³ HCl solution for 3 days. The solution to solid ratio was 100 cm³ g⁻¹ and the acid solution was replaced daily for a fresh one. The protonated sample was shaken moderately with a tetrabutylammonium hydroxide (TBAOH) solution at ambient temperature for more than two weeks. The dose of TBAOH was adjusted to be the equivalent of the exchangeable protons in the oxide. A translucent suspension was obtained after separating an unreacted residue in a small amount from the above mixture by centrifugation at 2000 rpm.

Substrates such as Si wafer and quartz glass plate were cleaned by dipping in HCl / CH₃OH (1:1) solution and then in conc-H₂SO₄ solution, after which they were immersed in an aqueous solution of poly(diallyldimethylammonium chloride) (pH = 9, 2.5 g dm⁻³) for 20 min to precoat the surface. Then, they were dipped in the colloidal suspension of negatively charged nanosheets (pH = 10, 0.3 g dm⁻³) for 20 min to

fabricate a monolayer film, in which the nanosheets lay flat to the substrate by the well-established self-assembly procedure (ref. 13).

Measurements and analysis. X-ray diffraction (XRD) data were collected using a Rigaku Rint 2000 powder diffractometer with Cu K α radiation ($\lambda = 0.15405$ nm). TEM observations and selected-area electron diffraction measurements were performed using a JEOL 1010 transmission electron microscope operated at 100 kV. Specimens were prepared by placing a drop of the colloidal suspension onto a holey carbon coated Cu grid. X-ray absorption near-edge structure spectra (XANES) for film and bulk samples were carried out under total reflection fluorescence mode and conventional transmission mode, respectively, at the Photon Factory BL-12C in the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK-PF). In-plane XRD analysis for a monolayer film of the nanosheets was performed with a four-axis diffractometer installed at the BL-6C in KEK-PF. A monochromatic X-ray ($\lambda = 0.13989$ nm) with horizontal divergence of 0.15° and vertical divergence of 0.30° restricted by conventional slits and a soller slit was struck to the sample surface below the critical angle of total external reflection. The divergence of the diffracted beam along the in-plane direction was restricted by a soller slit ($\sim 0.4^\circ$) placed in front of the detector. The diffracted X-ray was counted for three seconds at each sampling point (angular interval of 0.05°). A tapping-mode atomic force microscope (Seiko Instruments SPA400 AFM system) with a Si tip cantilever (20 N m^{-1}) was used to examine the topography of the nanosheets deposited on the Si substrate.

Chemical analysis. The powder sample was melted in a mixture of Na_2CO_3 and H_3BO_3 by heating. The cooled melt was dissolved with an aqueous solution of HCl and HF (3:1). The obtained solution was analyzed for Rb by atomic absorption spectrometry

(Varian Spectr AA-20) and for Ta by inductively coupled plasma atomic emission spectrometry (Jarrell Ash IRIS advantage). A weight loss up to 1273 K measured by thermogravimetry (Rigaku Thermo plus TG 8120) was used to estimate the water content.

Figure S1 XRD patterns for (a) starting material and (b) protonated form with Miller indices.

Both patterns except for a small peak at $2\theta = 26.6^\circ$ of the protonated form could be indexed based on the C-base centered monoclinic symmetry.

Figure S2 Ta L_{III}-edge XANES spectra for (a) RbTaO₃, (b) protonic tantalum oxide, (c) TaO₃ nanosheet and (d) Ta₂O₅.

All samples, (a)-(c), showed a sharp upsurge at 9880 eV in the white line region, which is characteristic of pentavalent tantalum ion (d) arising from dipole-allowed transitions from the core 2p to 5d states. This clearly indicates that chemical valence of tantalum ions remained unchanged in the process of the nanosheet synthesis.

Figure S3 Integrated peak intensity for the in-plane XRD pattern obtained from a monolayer of the TaO₃ nanosheets, (a) and a square of simulated structure factor with a scattering vector parallel to the TaO₃ single host layer, (b).

j	n	x	y
Ta1	0.5	0.000	0.190
Ta2	0.5	0.257	0.500
O1	1.0	0.101	0.166
O2	0.5	0.208	0.500
O3	1.0	0.122	0.342
O4	0.5	0.375	0.500

The TaO₃ nanosheet belongs to a two-dimensional space group of c2mm. An asymmetric unit includes two sites for tantalum atom and four sites for oxygen atom. The structure factor, $F(hk)$, with a scattering vector parallel to the sheet was calculated by the following equation:

$$F(hk) = \sum_j m_j f_j \exp[2\pi i \{hx_j + ky_j\}]$$

where m_j is site multiplicity, f_j is atomic scattering factor, and x_j, y_j are fractional coordinate for j th atoms. Atomic coordinates in the table are derived from the crystallographic data of RbTaO₃. The square of $F(hk)$ was further multiplied by the multiplicity of diffraction peaks and Debye-Waller factor, $\exp\{-0.5 \cdot (\sin\theta/\lambda)^2\}$, to obtain peak intensities. The close similarity in intensity distribution between observed and calculated data indicates that the holey layer architecture was preserved in the nanosheet.