Supporting Information


Epitaxy on Demand

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1 Detailed description of the experimental methods

1.1 Chemicals and materials

K$_2$CO$_3$ (purum p.a.; $\geq$ 99.0%) was purchased from Fluka. CaCO$_3$ (A.C.S. reagent, chelometric standard; $\geq$ 99.95%), Nb$_2$O$_5$ (trace metals basis; 99.99%) and MoO$_3$ (A.C.S. reagent; $\geq$ 99.5%) were obtained from Sigma-Aldrich. TiO$_2$ (technical; $\geq$ 99%) and Li$_2$CO$_3$ (purum; $\geq$ 99%) were supplied by Riedel-de Haën. Nitric acid (65% w/w aqueous solution) was purchased from Acros Organics, an ammonium fluoride etching mixture (AF 875-125, PURANAL) from Honeywell, and tetra-$n$-butylammonium hydroxide (TBAOH) (40% w/w aqueous solution) from Alfa Aesar. Because of the serious health hazards associated with handling of the NH$_4$F · HF mixture, the solution was used only in a fume hood inside a lab with an emergency hexafluorine washing station while wearing protective gloves, protective clothes and eye protection. All experiments that involved nitric acid were carried out in a fume hood. Ethanol (absolute, $\geq$ 99.8%) and acetone were acquired from Atlas & Assink Chemie and ultrapure water with a resistivity of 18.2 MΩ · cm was used. All chemicals were used as received without further purification.

Single crystal B-doped (100) Si wafers (grown by the Czochralski process) were purchased from Okmetic and single crystalline (001) and (110) SrTiO$_3$ substrates (grown by the Verneuil process) were acquired from CrysTec GmbH. During PLD a single crystalline target of SrTiO$_3$ was used, as well as a stoichiometric polycrystalline target of SrRuO$_3$ that was obtained from Praxair electronics.

1.2 Preparation of precursors and exfoliation into nanosheets

KCa$_2$Nb$_3$O$_{10}$ was prepared by mixing K$_2$CO$_3$ (2.81 g), CaCO$_3$ (7.41 g) and Nb$_2$O$_5$ (14.76 g) using mortar and pestle and annealing the mixed powders in a chamber furnace (Carbolite) inside a capped alumina crucible (100 ml Coors purchased from Sigma-Aldrich). The powder was heated from room temperature to 800°C at 5°C min$^{-1}$ and left at this temperature for 4 h, after which it was further heated at 0.5°C min$^{-1}$ to 1200°C at which it was kept for 10 h (the oven was allowed to cool to room temperature after this step at a maximum rate of 5°C min$^{-1}$). The powder was protonated by stirring it at 300 rpm inside a glass screw cap bottle in nitric acid (1.0 L, 5.00 M) for 72 h. The product was recovered by vacuum filtration (using Whatman No. 1450-055 filter paper), washed with a copious quantity of water (6 × 200 ml) and placed
inside a petri dish ($\varnothing = 150 \text{ mm}$) to allow it to dry at room temperature for 48 h.

To prepare $K_{0.8}[Ti_{1.73}Li_{0.27}]O_4$, $\text{TiO}_2$ (10.00 g), $K_2\text{CO}_3$ (16.70 g), $\text{Li}_2\text{CO}_3$ (0.722 g) and $\text{MoO}_3$ (13.16 g) were ground in ethanol (35 ml) for 48 h using milling balls of yttria-stabilized zirconia (YSZ). The slurry was then placed in a drying oven (Memmert) and kept overnight at 70$^\circ\text{C}$ after which the powder was calcined in the chamber furnace inside a closed Pt crucible. The powder was heated to 1150$^\circ\text{C}$ at 3$^\circ\text{C} \text{ min}^{-1}$ and kept at this temperature for 30 min. Then the powder was cooled to 950$^\circ\text{C}$ at 0.1$^\circ\text{C} \text{ min}^{-1}$ after which a maximum cooling rate of 5$^\circ\text{C} \text{ min}^{-1}$ was used to reach room temperature. The chunk was placed inside a glass screw cap bottle (500 ml) containing a stirring magnet and after addition of 200 ml water the bottle was vigorously shaken until the chunk fell apart. The suspension was then stirred at 300 rpm for 90 min, filtered by vacuum filtration (using glass microfiber filter GF8047 from ALBET LabScience) and washed 10× with water. The residue was added to the glass screw cap bottle and protonated in nitric acid (500 mL, 2.00 M) under constant stirring at 300 rpm during 96 h, in the course of which the solution was renewed every 24 h. Similar to the method used to obtain $\text{HCa}_2\text{Nb}_3\text{O}_{10} \cdot 1.5\text{H}_2\text{O}$ ($\text{HCNO}$), $\text{H}_{1.07}\text{Ti}_{1.73}\text{O}_4 \cdot \text{H}_2\text{O}$ ($\text{HTO}$) was recovered after vacuum filtration and drying.

The precursor powder of choice (0.4 g) was added to a screw cap bottle (250 ml polypropylene from Kautex) containing 100 ml water. The bottle was shaken vigorously for 1 min after which TBAOH (40% w/w; 479 µl in the case of HCNO and 845 µl in the case of HTO) was added and mixed with the dispersion by flipping the bottle upside-down (10×). The bottle was then placed horizontally on a rocking-shaker (ST3 from Assistent GmbH, Switzerland) operating at 30 oscillations per minute and was kept there for 9 (HCNO) or 6 days (HTO). The content of the bottle, including all precipitate, was then diluted in water (400 ml in the case of HCNO and 1900 ml in the case of HTO) and stored for 5 (HCNO) or 4 (HTO) days prior to use.

### 1.3 Langmuir-Blodgett depositions

Before conducting a Langmuir-Blodgett deposition, the surface of the substrate was cleaned by snow jetting (exposing the surface to a jet of supercritical CO$_2$ while the substrate is heated on a hot plate at 250$^\circ\text{C}$) and plasma cleaning (at 30 W for 15 min; Harrick plasma). Samples that already contained one or more layers of nanosheets and required an additional layer were cleaned by plasma only (for 2 min). Langmuir-Blodgett depositions were carried out in a double-barrier Langmuir trough with a vertical lifting configuration (MiniMicro from KSV NIMA, Finland) under a constant rate of compression
(3.0 mm min⁻¹). When Ca₂Nb₃O₁₀ nanosheets were to be deposited, a syringe was used to carefully extract 50 ml of the top part of the stock dispersion and add the dispersion to the Langmuir trough. For the deposition of Ti₀.₈₇O₂ nanosheets, a pipette (Eppendorf) was used to transfer the stock dispersion (4 × 5 ml) to a screw cap bottle (100 ml polypropylene from Kautex) after which water was added (30 ml; without further agitation). After 15 min of waiting, this dilution was poured into the Langmuir trough. After waiting for (another) 15 min, the cleaned substrate was clamped on the dipper and the Wilhelmy plate was hanged in place on the microbalance after completely immersing it in the dispersion. The dipper was then lowered to submerge the substrate in the liquid, and after again 15 min the microbalance was tared and movement of the barriers was initiated. The development of surface pressure was monitored (Figure S1) and compression was continued until the isotherm leveled off, indicating a dense monolayer film of nanosheets had formed on the surface of the liquid. Especially depending on the kind of nanosheets and age of the stock solution that was used, the required surface pressure for a high coverage was Π = 17 mN · m⁻¹ (Π = 20 mN · m⁻¹) for Ca₂Nb₃O₁₀ (Ti₀.₈₇O₂) nanosheets. By continuous movement of the barriers (3.0 mm min⁻¹) the surface pressure was maintained while the substrate was lifted out of the liquid at a constant rate of 1.0 mm min⁻¹ during which the monolayer was transferred to the substrate. Before conducting any further experiments other than topographic analysis by AFM, all samples were annealed in a microwave furnace (Microsynth, Milestone Srl) that was heated from room temperature to 600 °C at maximum power (1.0 kW) for 30 min.

Figure S1: Surface pressure isotherms of selected compression experiments performed prior to the Langmuir-Blodgett depositions.
Analysis of thermal stability of Ti$_{0.87}$O$_2$ nanosheets by XPS

X-ray photoelectron spectroscopy (XPS) was used to study changes of chemistry in the nanosheets and substrate by comparing the spectra of samples before and after thermal treatment, the results of which are displayed in Figure S2. Various changes were observed after heating a sample under deposition conditions. The intensity of the Si 2p peak of silicon bound to oxygen (around a binding energy of $BE \approx 104$ eV) clearly increased compared to that of bare Si (around $BE \approx 100$ eV), which means that the originally native oxide grew at elevated temperatures. At the same time, the intensity of the O 1s peak around $BE \approx 533$ eV did not show such increase, indicating that although the thickness of the SiO$_x$ layer increased, $x$ actually decreased. Small shifts to higher binding energy were observed in the Ti 2p peaks ($\Delta BE = +0.13 \pm 0.02$ eV) while the O 1s and Si 2p peaks from the native oxide layer shifted to lower binding energies (the peaks shifted by $\Delta BE = -0.26 \pm 0.11$ eV and $\Delta BE = -0.25 \pm 0.07$ eV, respectively). No significant peak shifts were found for the O 1s peak of the nanosheets and the Si 2p peaks of the substrate, and no signs of formation of silicides were found. Also, no significant change of the atomic ratio in the titania nanosheets was found before and after heating. Based on these results we concluded that the native oxide on the silicon substrate may have formed silicates with the titania nanosheets, as the spectral shifts indicate (small) changes of chemistry in the nanosheets and SiO$_x$ layer.

![Figure S2: XPS spectra obtained from scanning two samples at two different emission angles around the O 1s, Ti 2p and Si 2p peaks. Both samples consisted of a single layer of Ti$_{0.87}$O$_2$ nanosheets on a Si substrate with oxide layer, of which one was measured directly after Langmuir-Blodgett deposition of the nanosheets and the other after bringing the sample to deposition conditions.](image-url)
Figure S3: Schematical representation of the three samples made with seed layers of nanosheets, as discussed in the main article.

Figure S4: Tapping mode AFM height images of films deposited on Si substrates containing monolayers of Ca$_2$Nb$_3$O$_{10}$ nanosheets, recorded after deposition of the buffer layer of SrTiO$_3$ (top) and after growth of the buffer layer followed by growth of approximately 14 nm SrRuO$_3$ (bottom). In the different experiments, the thickness of the buffer layer was varied between 0 and 44 unit cells (U.C.) as indicated above the AFM images. In all images a horizontal line can be found, marking the location from which the height profile in the corresponding inset was obtained.
Figure S5: X-ray reflectivity scans (in red) and fits (in blue) for the films of SrRuO$_3$|SrTiO$_3$ on (a) a single layer of Ca$_2$Nb$_3$O$_{10}$ and (b) two layers of Ti$_{0.87}$O$_2$ nanosheets.

Figure S6: High-resolution SEM images of a pattern of 25 $\mu$m wide lines of Ca$_2$Nb$_3$O$_{10}$ nanosheets on top of two layers of Ti$_{0.87}$O$_2$ nanosheets supported on a Si substrate, measured using (a) an in-lens and (b) an energy selective backscatter (ESB) detector. The latter detector is particularly sensitive to compositional contrast, in the present case to the different atomic numbers of Ti and Nb.
Figure S7 (preceding page): Analysis and characterization of fully oriented films of SrRuO$_3$ on SrTiO$_3$ (001)$_c$ and (110)$_c$, deposited under the same conditions as those on Si covered with nanosheets. Course of the intensity and FWHM of the RHEED specular spot during initial growth on a (a) (001)$_c$ oriented and (b) (110)$_c$ oriented substrate. (c) Topographical and (d) structural analysis of the (001)$_c$ oriented thin film by tapping mode AFM and XRD, respectively, and (e,f) similar analyses performed on the other film. The lattice parameters of the (001)$_c$ oriented film were refined to $a_o = 5.57$ Å, $b_o = 5.55$ Å, $c_o = 7.80$ Å, $\alpha = 89.9^\circ$, $\beta = 89.9^\circ$, $\gamma = 89.2^\circ$ and that of the (110)$_c$ oriented film to $a_o = 5.54$ Å, $b_o = 5.53$ Å, $c_o = 7.86$ Å, $\alpha = 90.6^\circ$, $\beta = 89.3^\circ$, $\gamma = 90.5^\circ$. Magnetic and electrical characterization of the (g-i) (001)$_c$ and (j-l) (110)$_c$ oriented films include (g,j) hysteresis loops measured at 10 K, (h,k) temperature dependence of saturation magnetization together with the best fit to Brillouin functions obtained when total angular momentum quantum number $J = 4$ (the different curves were obtained for $J = 1, 2, 4, \infty$, where $J$ increases in the direction of the arrow), and (i,l) sheet resistivity versus temperature.