

Supplementary Information

A perfectly oriented, free-standing and transparent titania nanosheet film with the band gap of a monolayer

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Materials

Cesium carbonate (Cs_2CO_3 , 95.0-102.0%, FUJIFILM Wako Pure Chemical Corporation), titanium oxide (TiO_2 , anatase form, 98.5%, FUJIFILM Wako Pure Chemical Corporation), tetrabutylammonium hydroxide ($(\text{C}_4\text{H}_9)_4\text{N}^+\text{OH}^-$, TBA, 10% in water, FUJIFILM Wako Pure Chemical Corporation), ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.5%, FUJIFILM Wako Pure Chemical Corporation), sodium chloride (NaCl , 99.8%, FUJIFILM Wako Pure Chemical Corporation), sodium sulfate (Na_2SO_4 , 99.0%, FUJIFILM Wako Pure Chemical Corporation), methanol (CH_3OH , 99.8%, FUJIFILM Wako Pure Chemical Corporation), acetone (CH_3COCH_3 , 99.5%, FUJIFILM Wako Pure Chemical Corporation), and Milli-Q deionized water ($\geq 18.2 \text{ M}\Omega$) were used for all experiments.

Preparation of condensed titania nanosheet suspension

Cs_2CO_3 and TiO_2 ($\text{Cs}/\text{Ti} = 0.81/1.81$ molar ratio) were ground finely in an agate mortar for 15 minutes, and then the mixed powder was annealed at $800 \text{ }^\circ\text{C}$ for 20 h ($\text{Cs}_{0.68}\text{Ti}_{1.83}\text{O}_4$).^{S1} 0.958 g of $\text{Cs}_{0.68}\text{Ti}_{1.83}\text{O}_4$ was placed in 100 mL of 1 M HCl ($\text{H}^+/\text{Cs}^+ = 40/1$) for 3 days to exchange interlayer Cs^+ to H^+ ($\text{H}_{0.68}\text{Ti}_{1.83}\text{O}_4 \cdot x\text{H}_2\text{O}$). The acid was replaced with a fresh solution each day. The $\text{H}_{0.68}\text{Ti}_{1.83}\text{O}_4 \cdot x\text{H}_2\text{O} + \text{HCl}$ suspension was centrifuged at 3500 rpm for 15 min, followed by removal of the supernatant liquid. The precipitate was rinsed with deionized water 5-6 times to remove excessive H^+ . The rinsed $\text{H}_{0.68}\text{Ti}_{1.83}\text{O}_4 \cdot x\text{H}_2\text{O}$ was dried at room temperature, and 0.39 g of the powder was added into 500 mL of 0.025 M TBA ($\text{TBA}^+/\text{H}^+ \sim 8/1$). The $\text{H}_{0.68}\text{Ti}_{1.83}\text{O}_4 \cdot x\text{H}_2\text{O} + \text{TBA}$ suspension was ultrasonicated for over 9 h to promote delamination of the titania ($\text{Ti}_{0.91}\text{O}_2$) nanosheets. The titania nanosheet suspension was centrifuged at 3500 rpm for 15 min to remove unexfoliated material. The supernatant was centrifuged at 12000 rpm for 60 min and the supernatant was replaced with deionized water. The precipitate was dispersed by ultrasonication, the suspension was centrifuged at 12000 rpm again and the precipitate was dispersed in ethanol or acetone. 3.5 and 20 mg/mL dispersions were used for the following spin-coating process.

Spin coating process

The titania nanosheet suspension was dropped onto a Si wafer or quartz glass plate, and then the wafer was processed by 3-step rotation as follows: (i) 200 rpm for 5 s, (ii) 0 rpm for 3 s, (iii) 200-2000 rpm for 5 s. After coating, the substrate was heated at $\sim 100 \text{ }^\circ\text{C}$ for 5-10 s. This process was repeated for 2-25 cycles.

The quartz glass plate was used for estimating the band gap of the titania coatings. The Si wafer was used for preparation of the free-standing titania film, and other measurements including XRD and FE-SEM.

Annealing process

The titania nanosheet coating was annealed at $200 \text{ }^\circ\text{C}$ before XRD and FE-SEM measurements to remove interlayer water and to estimate number of layers. Higher annealing temperatures ($400\text{-}600 \text{ }^\circ\text{C}$ for 3 h) were used to investigate the orientation after the phase transformation from the titania nanosheet to anatase TiO_2 . The titania nanosheet free-standing film was prepared without any annealing processes.

Detachment of titania nanosheet film from Si wafer

The titania nanosheet coating prepared with 10 coating cycles at 500 rpm was immersed in 3 M NaCl for 15-30 h to exchange the interlayer TBA^+ with Na^+ . The NaCl solution was replaced with deionized water. The titania coating was carefully detached from the Si wafer (free-standing titania film). The free-standing film was transferred onto an aluminum plate with 20x20 mm window for measurement of UV-vis absorption and ITO coated quartz glass for electrochemical measurements. Photographs of the detachment process of the coating are shown in Figure S9b.

Characterization

The orientation of titania films was confirmed by in-plane ($2\theta\chi$) and out-of-plane ($2\theta/\theta$) X-ray diffraction patterns (XRD, SmartLab 1.2 kW $\text{CuK}\alpha$ and $\text{K}\beta$ X-ray diffractometer, Rigaku Corporation). The cross-sectional structure of the coating was observed by field-emission secondary electron microscope (FE-SEM, SU8000,

Hitachi High-technologies Corporation). The band gap and the refractive index of the coating was estimated by ultraviolet-visible absorption/reflectance spectra (UV-vis spectra, V-550, JASCO Corporation). Electrochemical measurements were performed by IVIUM Compactstat (Ivium Technologies) in 0.5 M Na₂SO₄ + 0.1 M CH₃OH aqueous solution (pH = 6.5) with Ag/AgCl reference electrode (+0.199 V vs. NHE) and Pt wire counter electrode. A 300 W Xe lamp with no optical filter (MAX-302, Asahi spectra) was used as a UV light source.

Determination of refractive index of the oriented titania coating from visible reflectance spectrum

The relationship between the refractive index (n) and the wavelength at maximal reflectance (λ) is showed by:

$$2nT = m\lambda \dots (1)$$

where T is the thickness of the titania coating, $m = 1$ for all samples.

Determination of band structure of the free-standing titania film by Mott-Schottky plot

Mott-Schottky plot was used to determine the flat band potential (U_{fb}) and the carrier density (N_D) of the free-standing titania film. The relationship between U_{fb} and the capacitance (C) is showed by:

$$1/C^2 = \frac{2}{N_D \epsilon_0 \epsilon_r q} \left(U - U_{fb} - \frac{k_B T}{q} \right) \dots (2)$$

where ϵ_0 is the dielectric constant of vacuum (8.854×10^{-12} F/m), ϵ_r is the relative dielectric constant, q is the elementary charge (1.602×10^{-19} C), U is the applied potential, k_B is the Boltzmann's constant (1.381×10^{-23} J/K), T is the absolute temperature (298 K). N_D and U_{fb} are determined using formula obtained from the electrochemical measurement ($1/C^2 = 1.89 \times 10^{10} U + 1.78 \times 10^{10}$).

When $1/C^2 = 0$ and $\epsilon_r = 125$ (ref. S2),

$$U_{fb} = U|_{1/C^2=0} - k_B T/q = -0.97 \text{ V vs. Ag/AgCl} = -0.77 \text{ V vs. NHE} \dots (3)$$

$$2/N_D \epsilon_0 \epsilon_r q = 1.89 \times 10^{10} \therefore N_D = 5.97 \times 10^{19} \text{ cm}^{-3} \dots (4)$$

The effective density of state (N_C) of the n-type semiconductor is determined by:

$$N_C = 2 \left(\frac{2\pi m_e k_B T}{h^2} \right)^{3/2} \dots (5)$$

where m_e is the effective mass of electron, h is the Planck's constant (6.626×10^{-34} Js). When m_e is $9.0 \times 9.109 \times 10^{-31}$ kg (ref. S3),

$$N_C = 6.71 \times 10^{20} \text{ cm}^{-3} \dots (6)$$

The energy of conduction band minimum (CBM, E_C) is determined by the formula of N_C :

$$E_C = E_F - k_B T \ln \left(\frac{N_D}{N_C} \right) \dots (7)$$

where E_F is the fermi level. When E_F is equal to the energy of the flat band potential (E_{fb}), E_C is calculated as:

$$E_C \sim E_{fb} - k_B T \ln \left(\frac{N_D}{N_C} \right) = 0.77 + 0.06 \text{ eV} = 0.83 \text{ eV} \dots (8)$$

The energy of valence band maximum (E_V , VBM) is calculated using the band gap (E_G):

$$E_G = E_C - E_V \therefore E_V = 0.83 - 3.76 = -2.93 \text{ eV} \dots (9)$$

These values correspond to the potentials of CBM and VBM level at **-0.83 V** and **2.93 V** (vs. NHE), respectively.

Estimation of the thickness of the free-standing titania film

The thickness of the free-standing film was estimated from the formulae obtained in Figure S2b:

$$T = 12245 \omega^{-0.734} \dots (10)$$

where T is the thickness of the coating (nm) and ω is the rotating speed (rpms). All samples in Figure S2b were prepared with 6 coating cycles, so that the formula (10) could be written as:

$$T = 12245 \omega^{-0.734} \times \frac{N}{6} \dots (11)$$

The free-standing film was prepared at 500 rpm with 10 coating cycles. The thickness is estimated as:

$$T = 12245 \times 500^{-0.734} \times \frac{10}{6} = 213 \text{ nm} \dots (12)$$

Figures

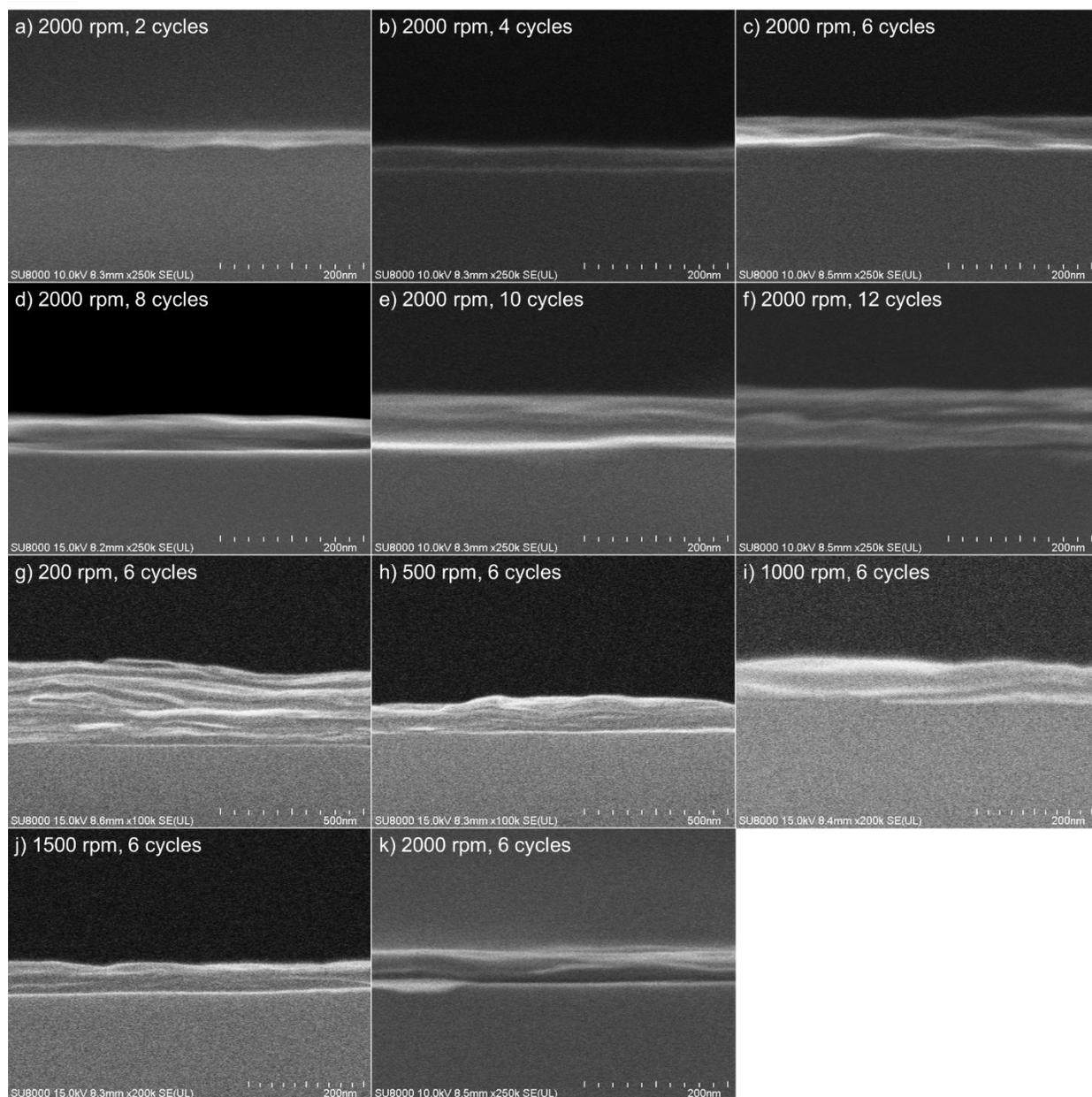


Figure S1. FE-SEM images of the titania nanosheet coating on Si wafer with (a-f) different numbers of coating cycles at 2000 rpm and at (g-k) different rotation speeds with 6 coating cycles.

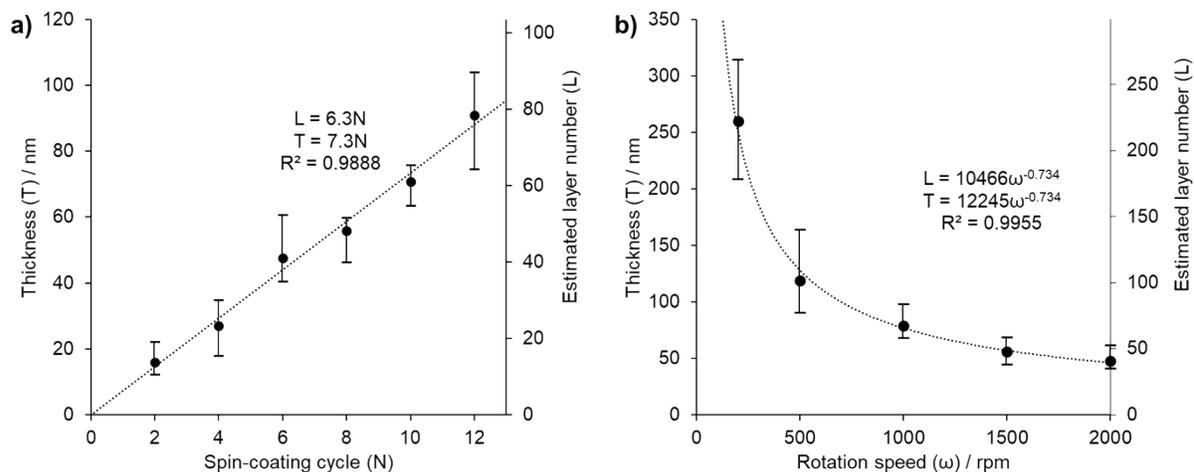


Figure S2. Relationship between thickness of titania nanosheet coating and a) number of coating cycles (2000 rpm), b) rotation speeds (6 coating cycles).

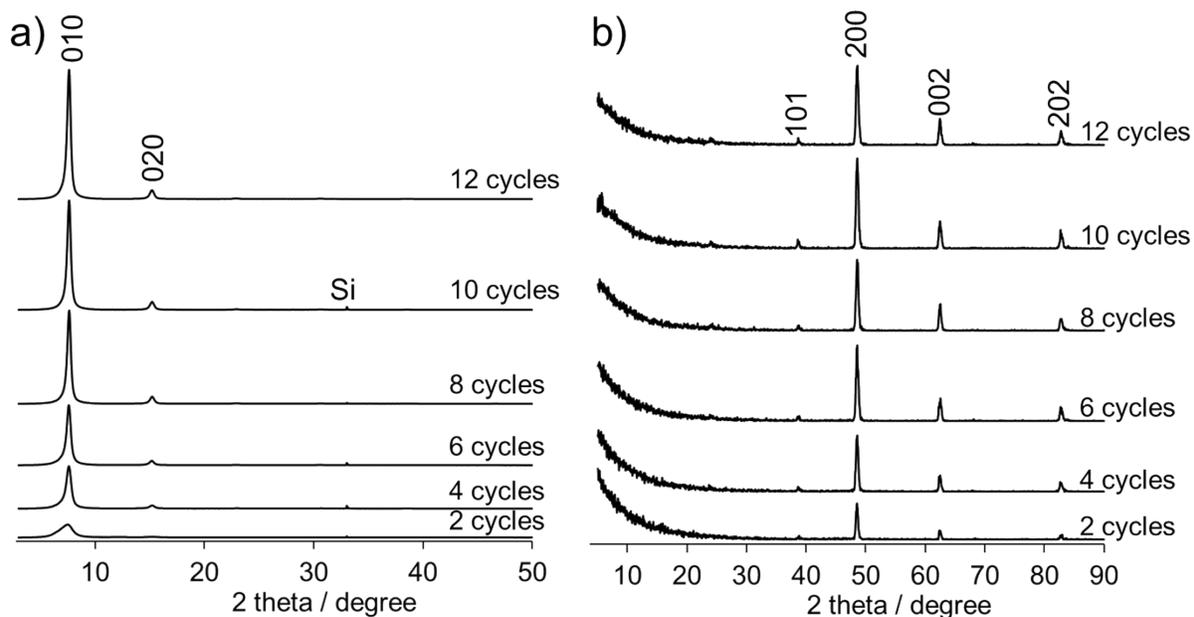


Figure S3. a) Out-of-plane ($2\theta/\theta$ scan) and b) in-plane ($2\theta\chi$ scan) XRD patterns of titania nanosheet coatings prepared with different numbers of coating cycles (2, 4, 6, 8, 10, and 12 cycles) at 2000 rpm.

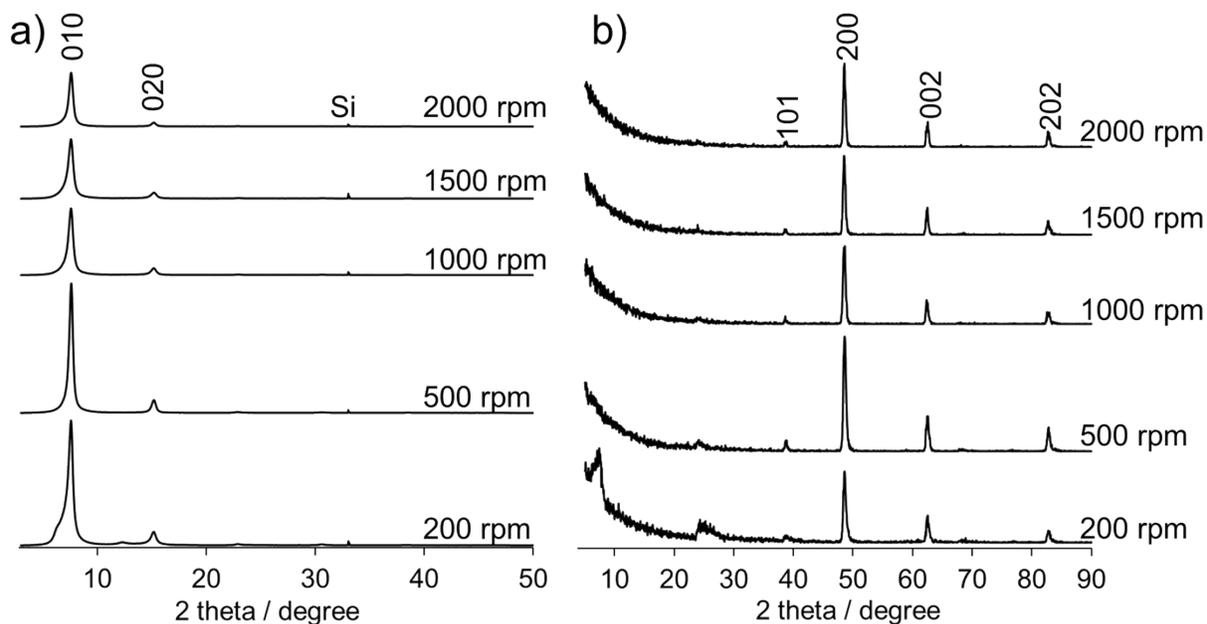


Figure S4. a) Out-of-plane ($2\theta/\theta$) and b) in-plane ($2\theta\chi$) XRD patterns of titania nanosheet coatings prepared at different rotation speeds (200, 500, 1000, 1500, and 2000 rpm) with 6 coating cycles.

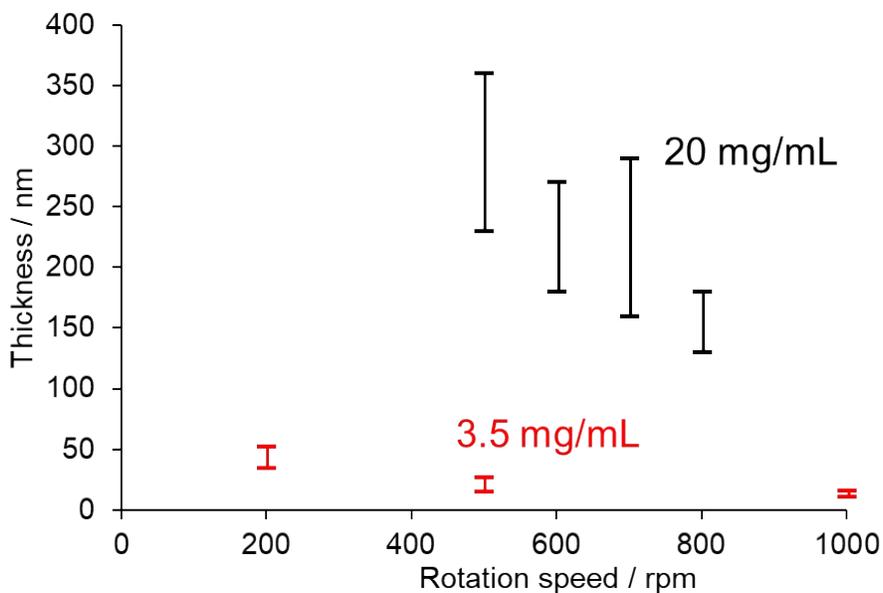


Figure S5. Thickness of titania nanosheet coatings prepared with nanosheet suspensions of different concentrations (3.5 and 20 mg/mL) at 200-1000 rpm.

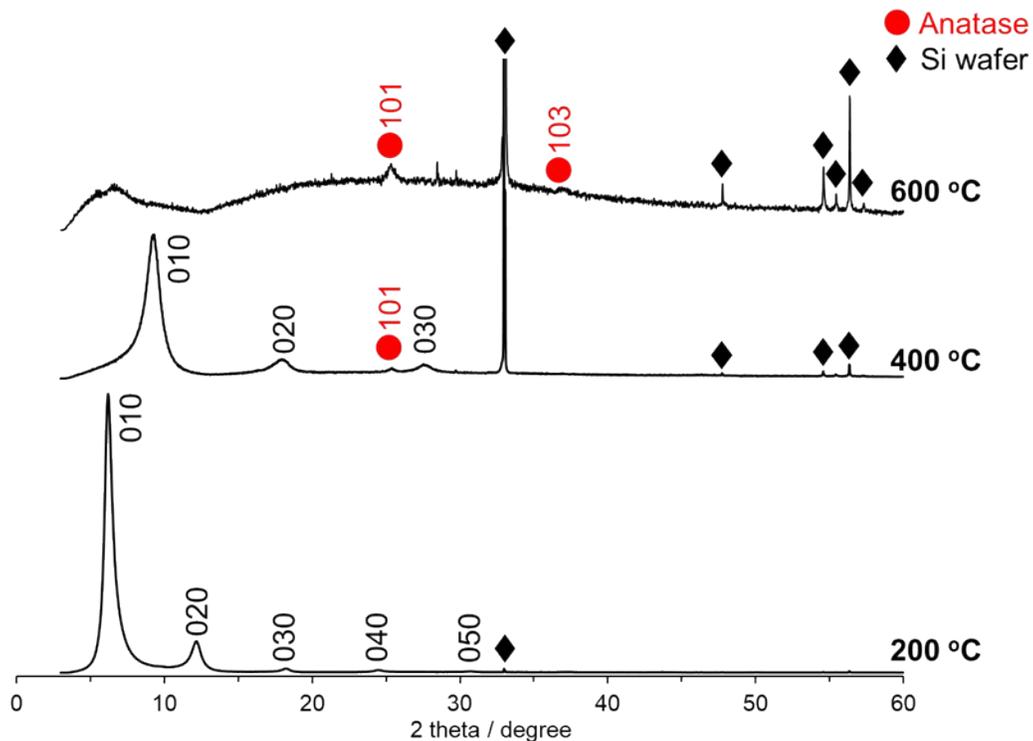


Figure S6. Out-of-plane XRD pattern ($2\theta/\theta$ scan) of 200, 400, and 600 °C annealed titania nanosheet coatings on Si wafer.

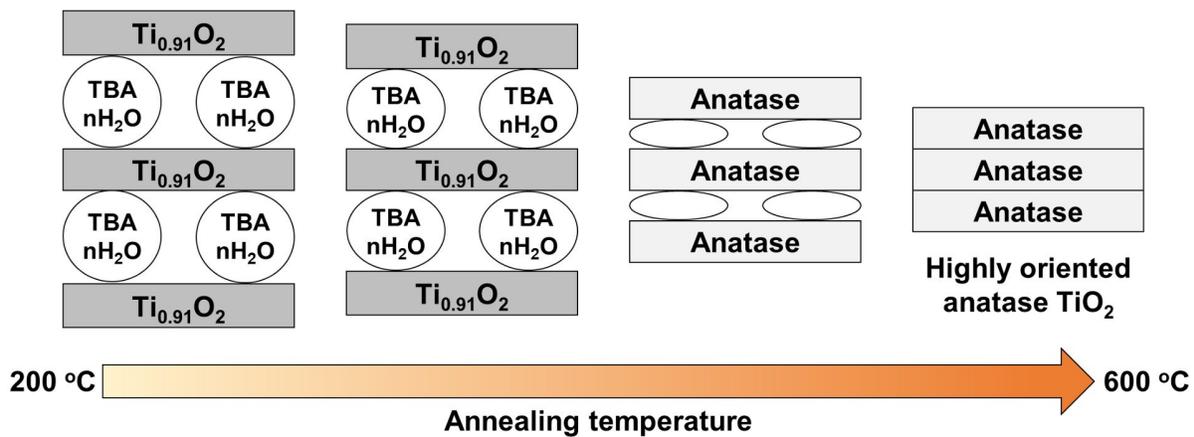


Figure S7. Schematic illustration showing the phase transformation of the titania ($\text{Ti}_{0.91}\text{O}_2$) nanosheet coating under annealing at 200-600 °C.

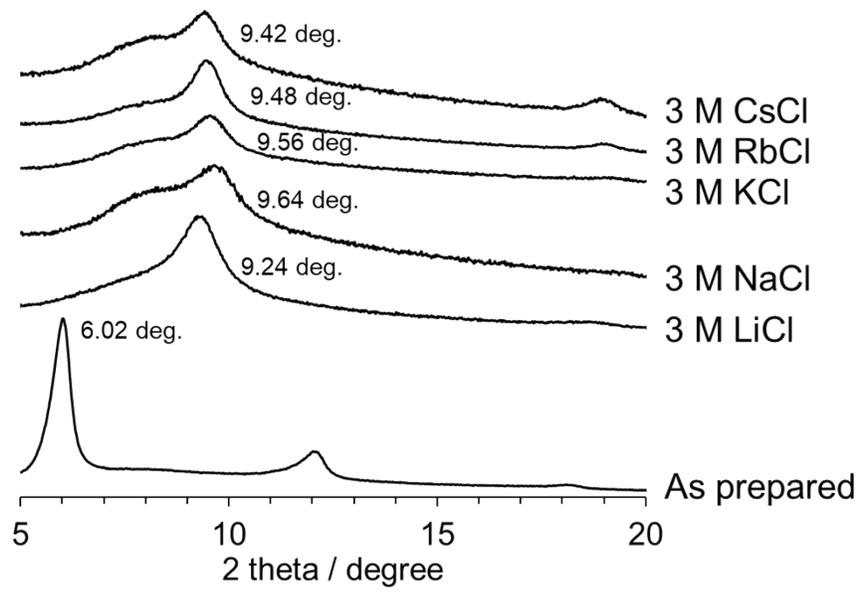


Figure S8. Out-of-plane XRD patterns of titania nanosheet coatings on Si wafer before (as prepared) and after immersion in 3 M LiCl, 3 M NaCl, 3 M KCl, 3 M RbCl, and 3 M CsCl.

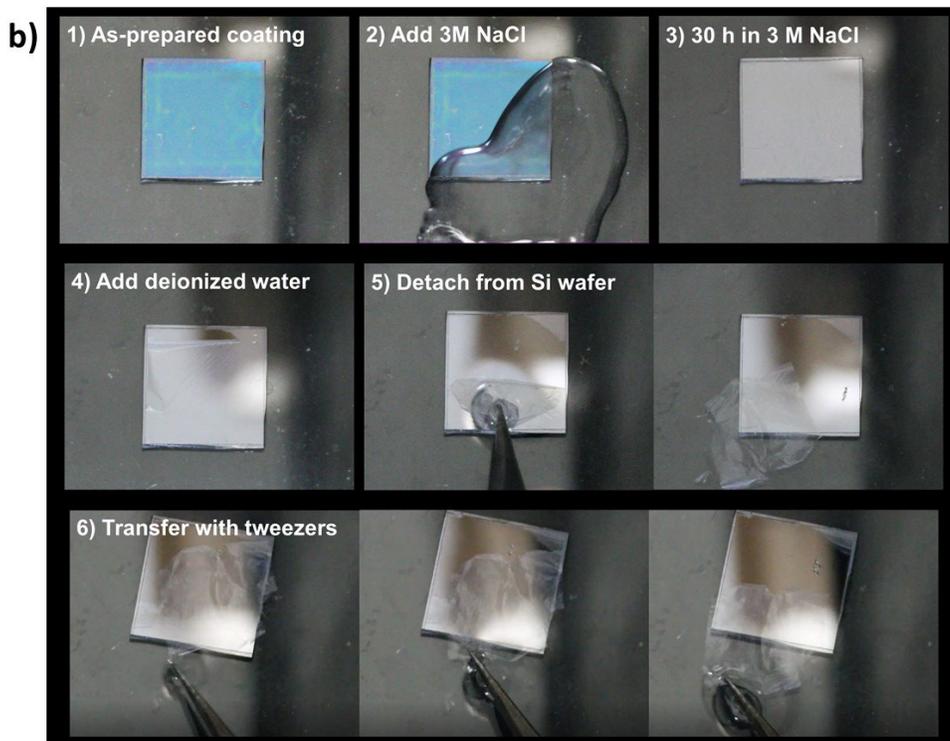
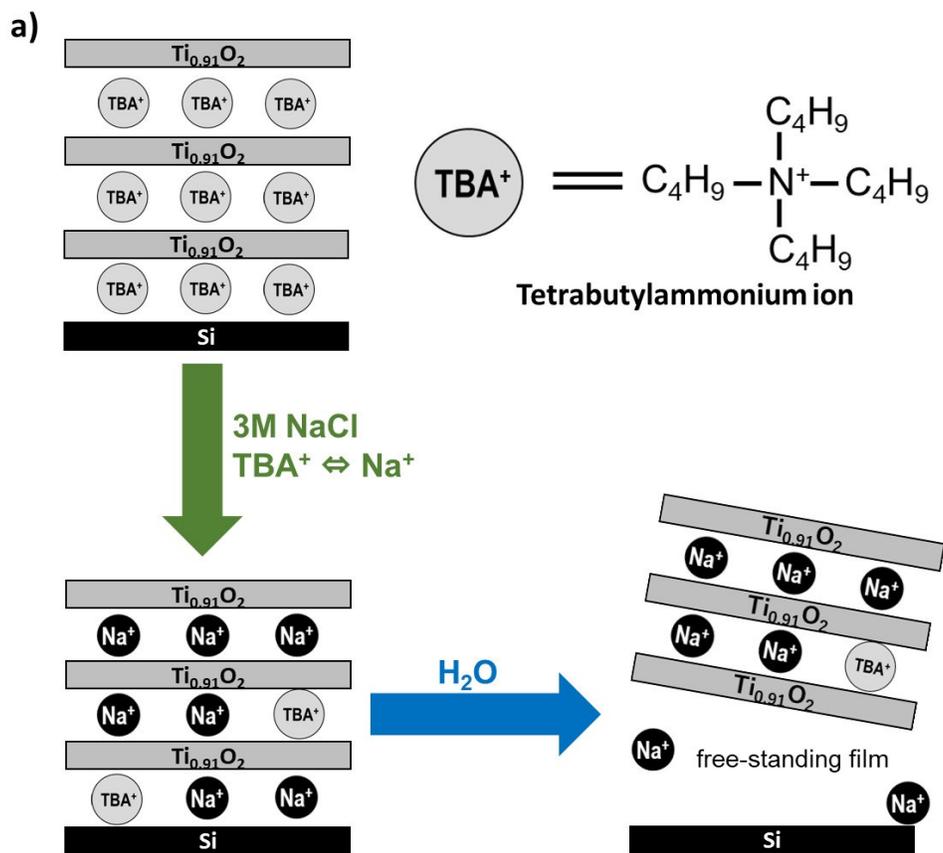


Figure S9. a) Schematic illustration and b) pictures showing the detachment process of the titania coating.

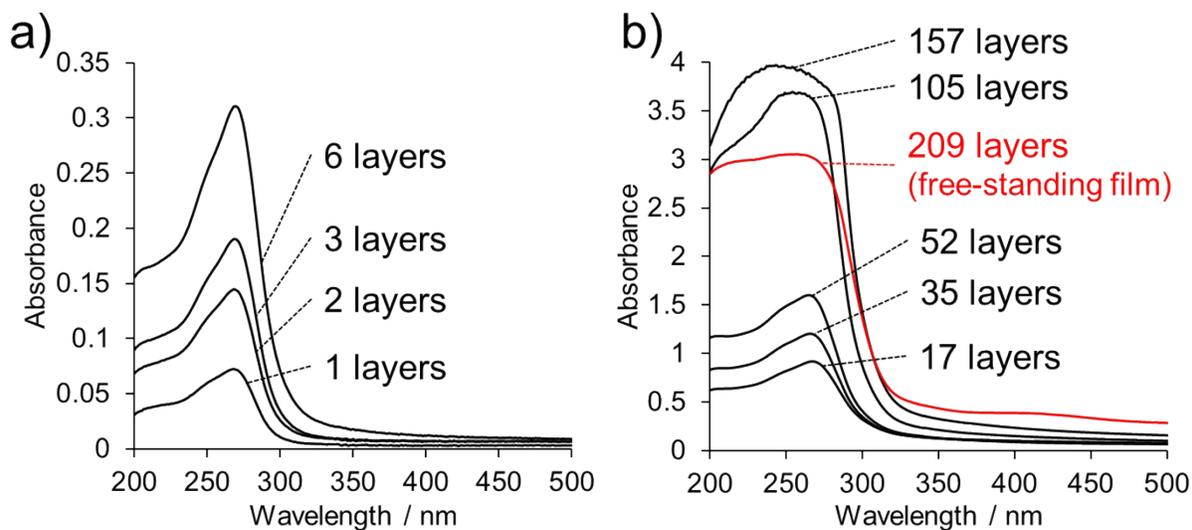


Figure S10. UV-vis absorption spectra of titania nanosheet coatings with different numbers of layers.

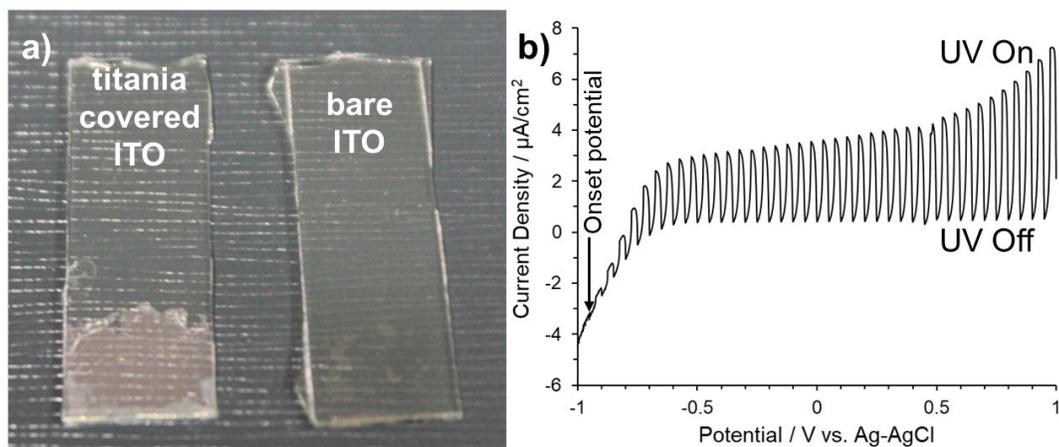


Figure S11. a) Photograph of free-standing titania film transferred onto an ITO coated quartz glass. b) Current-potential curve of the free-standing titania film on ITO glass in 0.5 M Na_2SO_4 + 0.1 M CH_3OH under chopped UV light irradiation.

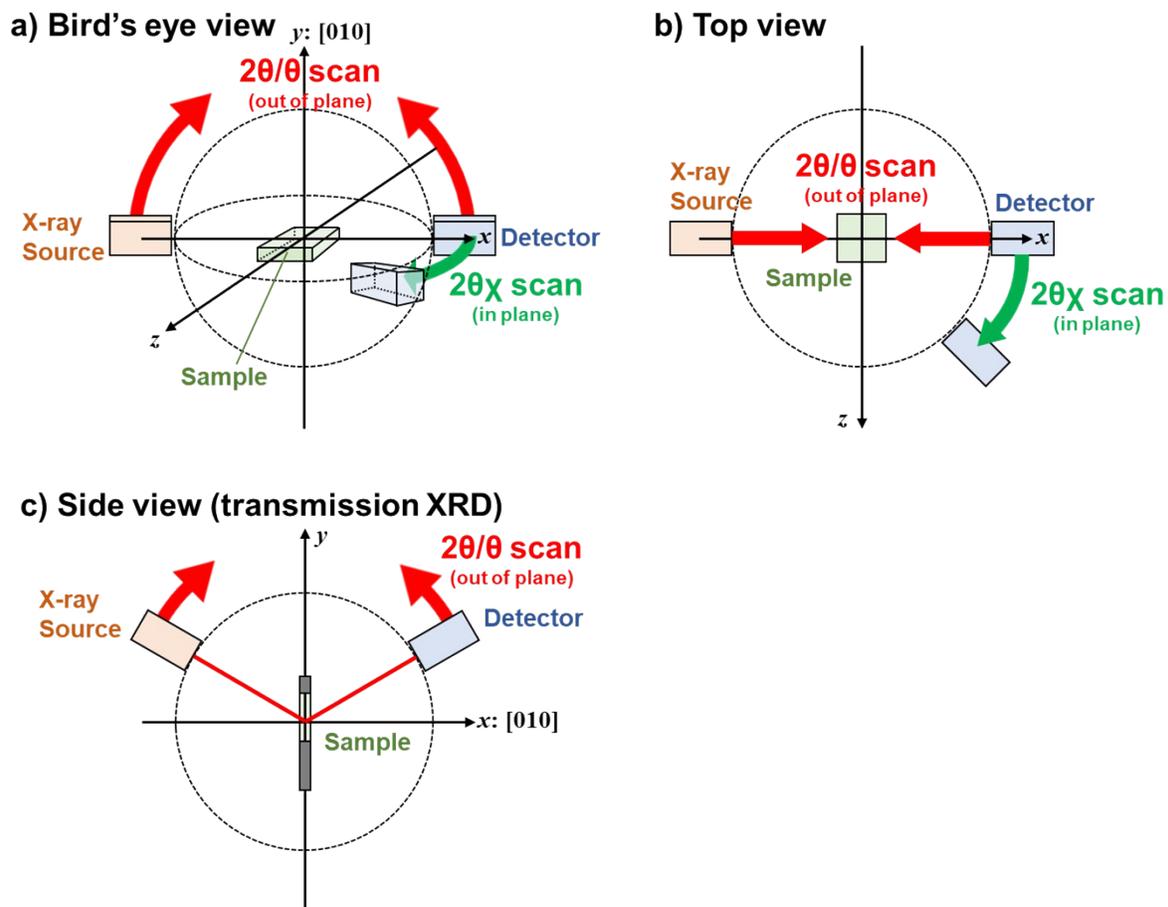


Figure S12. Schematic illustration showing the geometries of out-of-plane ($2\theta/\theta$ scan) and in-plane ($2\theta\chi$ scan) XRD measurements. a) Bird's eye view, b) top view, and c) side view (transmission XRD).

References

- S1) T. Sasaki, M. Watanabe, H. Hashizume, H. Yamada H. Nakazawa, *J. Am. Chem. Soc.* 1996, **118**, 8329.
- S2) M. Osada, T. Sasaki, *Adv. Mater.*, 2012, **24**, 210.
- S3) N. Sakai, Y. Ebina, K. Takada, T. Sasaki, *J. Am. Chem. Soc.* 2004, **126**, 5851.