

Supporting Information

Structure identification of Ti(IV) clusters in low-temperature TiO₂ crystallization: creating high-surface area brush-shaped rutile TiO₂

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Experimental

Chemicals

CH₃OH (Primepure, 99.9 %) and NaOH (97.0 %) were used as purchased from KANTO CHEMICAL. Titanium(IV) chloride solution (Ti: 16.0 %~17.0 %) diluted with water was purchased from Wako and used as purchased. H₂O (resistivity: 18.2 MΩ•cm) obtained using a Milli-Q[®] integral water purification system was used for the Ti(IV) hydrolysis reactions.

Synthesis of TiO₂ crystals (LTC-1)

NaOH (1.86 g) was dissolved in the aqueous solvent mixture of CH₃OH (250 ml) and H₂O (100 ml) in a 500 ml measuring flask. A TiCl₄ solution (57.5 g) prepared separately in a 100 ml beaker was then added dropwise with vigorous stirring. The volume of the mixture was adjusted to be 500 ml with H₂O. For the further reaction, the temperature in the reaction vessel was maintained at 27°C in a temperature-controlled room (see Figure S1). The white suspension was further reacted with stirring to become a transparent solution within 24 h. After 7 days of reaction, the crystalline-TiO₂ was collected by a centrifuge separator at 4500 rpm and 10 min and washed with H₂O. The white powder (with a yield of ~1 g) was obtained after drying in air.

EDX analysis of LTC-1 showed the significant decrease of Na and Cl contents after washing with H₂O. These contents changed from Na: 2% and Cl: 3% to Na: <0.1% and Cl: 1% for LTC-1.

Synthesis of TiO₂ crystals (LTC-2)

NaOH (1.86 g) was dissolved in H₂O (350 ml) in a 500 ml measuring flask. The hydrolysis was carried out in a way similar to that of LTC-1. After 72h of reaction, the crystalline-TiO₂ was collected and the obtained white powder was dried in air (with a yield of ~ 15g).

Na and Cl contents for LTC-2 after washing was Na: 0% (not detected) and Cl: 1%.

Structure characterization of Ti clusters and TiO₂ nanocrystals

LTC-1 and LTC-2 were characterized using X-ray diffraction, scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-TEM). These measurements were performed on a Rigaku RINT-Ultima/PC with monochromated Cu K α radiation, HITACHI S-4800, and JEM-2100, respectively. The XRD pattern of the Ti(IV) cluster was also obtained by a Rigaku RINT-Ultima/PC. EDX and MALDI-TOF mass spectra of Ti(IV) clusters were obtained by using

HITACHI S-4800, SHIMAZU AXIMA-Resinace, respectively. IR measurements of Ti(IV) clusters of Ti(IV) clusters were carried out on PerkinElmer Spectrum 400 FT-IR, FT-NIR. The BET surface area was evaluated by N₂ physisorption at 77K using a Micrometrics Tristar 3020.

Computational calculations

Optimization of Ti(IV) cluster structures was performed using DFT at the B3LYP/6-31G* level with Spartan '16 package, Wavefunction Inc. No constraints were applied in the calculations. The typical results of another isomer are shown in Fig. S11. A similar electron density distribution as seen in Figure 2 was obtained.

Assembly of electrochemical cells and characterization of photoanode property

A F-doped SnO₂ coated glass substrate, FTO (13Ω/□, Nippon Sheet Glass Co. Ltd.) was used for preparing the photoanode. A mixture of 8 ml ethanol (99.5%, Wako), 0.07 g HCl (35-37%, Wako) and 0.7 g titanium tetraisopropoxide (95%, Wako) was deposited on the top of the FTO by a spin-coating method with a speed of 1000 rpm for 30 s and 1500 rpm for 30 s. The TiO₂ particles were mixed with H₂O (20 wt%) and treated in an ultrasonicator, BRANSON (YAMATO 1510) to disperse the TiO₂ particles. A layer of TiO₂ was then deposited on the coated FTO substrate by spin coating the dispersed TiO₂ sample one time. The substrates were annealed at 150°C for 1 hour.

The TiO₂ film was then immersed in a solution of indoline dye D205 (Chemicrea Co., Ltd). The solvent mixture consisted of acetonitrile (super dehydrated, Wako) and *t*-butyl alcohol (Wako) with the volume ratio of 1:1. The dye adsorption was carried out at 25°C in dark conditions. The dye adsorption time was 4h and dye concentration was 0.2 mM. Pt-sputtered FTO glass was used as a counter electrode. The photo-electrode and counter electrode were then assembled into a sandwich-type cell with an active area of 5 mm × 6 mm. The electrolyte solution consisted of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (Wako), 0.1 M LiI (Wako), 0.05 M I₂ (Wako), and 0.05 M 4-*t*-butylpyridine (Aldrich) using 3-methoxypropionitrile (Wako) as a solvent. The electrolyte was introduced into the cell using a vacuum backfilling method.

The film thickness of the porous TiO₂ was estimated with KEYENCE VE-7800. The reflectance spectra were measured by using HITACHI U-4000 Spectrophotometer. The performance of photon-to-electricity conversions was examined under AM 1.5 simulated sunlight (100 mW/ cm²) using Yamashita Denso YSS-80A using HOKUTO DENKO Automatic Polarization System HSV-110. A black mask (4 mm × 5 mm) was used to regulate the active area of the device. Electrochemical impedance analysis was carried out by using AMETEK VersaSTAT 3.

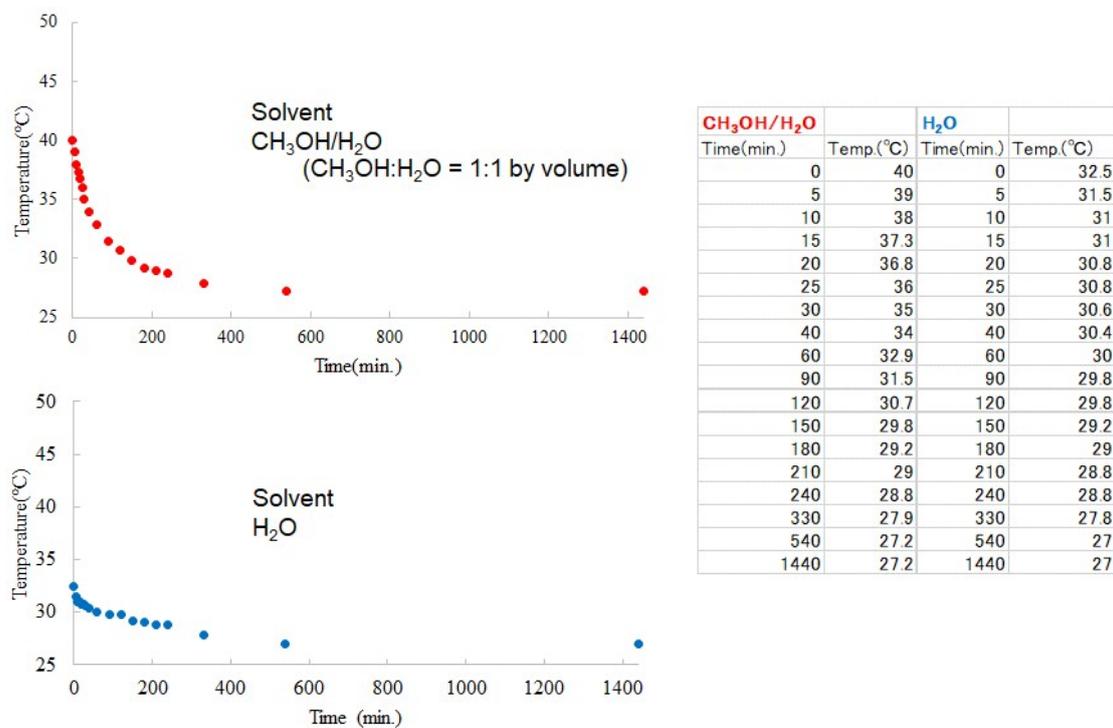


Fig. S1: Temperature changes in the reaction vessel at given times.

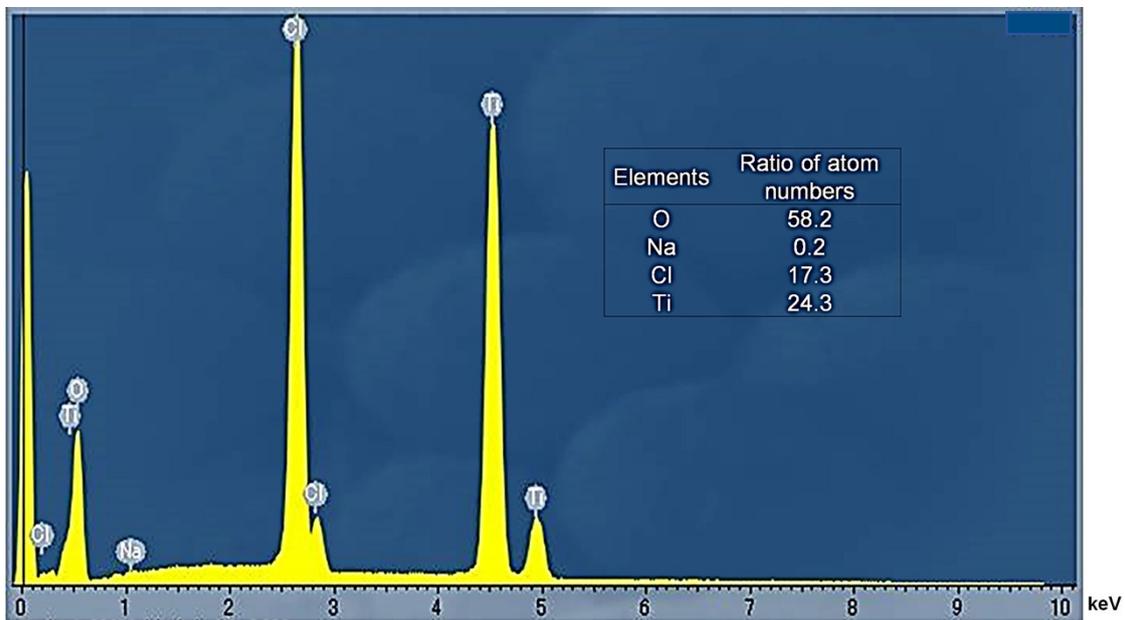


Fig. S2 EDX data of the Ti(IV) intermediate compounds produced after 24h of room temperature wet-synthesis at $27\pm 2^\circ\text{C}$ in $\text{CH}_3\text{OH}:\text{H}_2\text{O} = 1:1(\text{v}:\text{v})$.

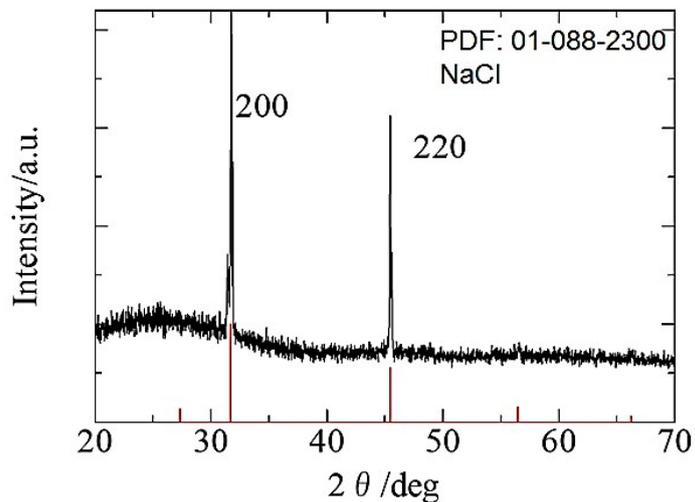


Fig. S3 Powder XRD pattern of the mixture of amorphous Ti(IV) precursor and co-crystallized NaCl that was produced after 24h of room temperature wet-synthesis at $27\pm 2^\circ\text{C}$ in $\text{CH}_3\text{OH}:\text{H}_2\text{O} = 1:1(\text{v}:\text{v})$.

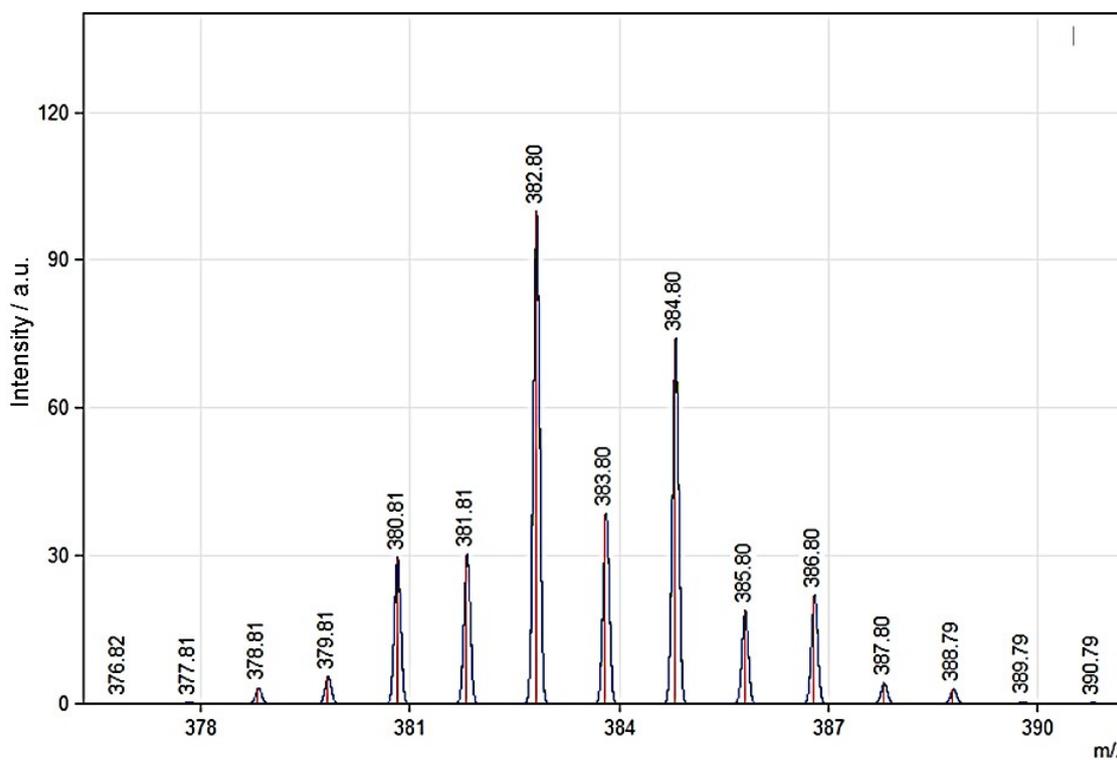


Fig. S4 Theoretical isotopic pattern of the ionized species, $[\text{Ti}_3\text{Cl}_2(\text{O})(\text{OH})_9]^+$, (with calculated m/z of 382.80).

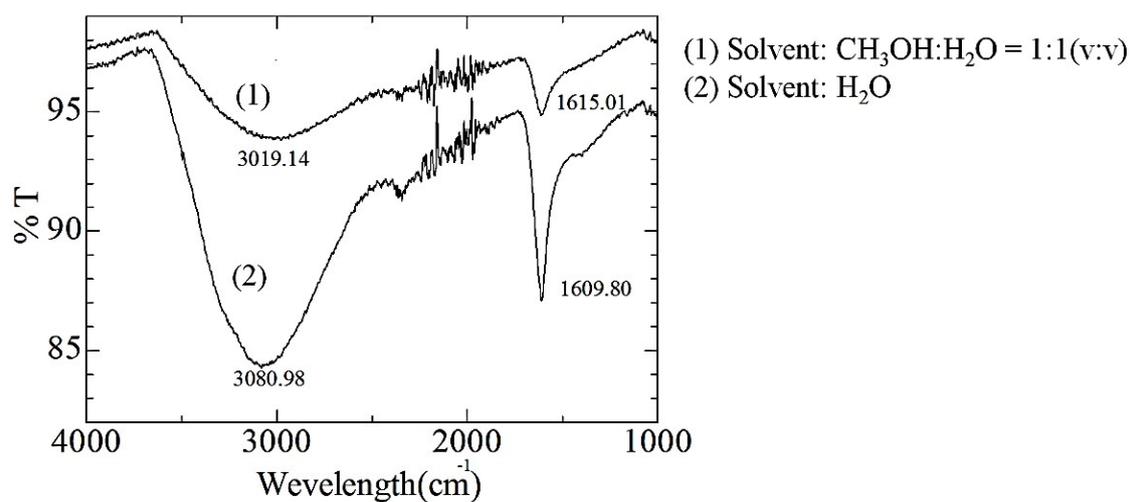


Fig. S5 IR spectra of the Ti(IV) intermediate compounds.

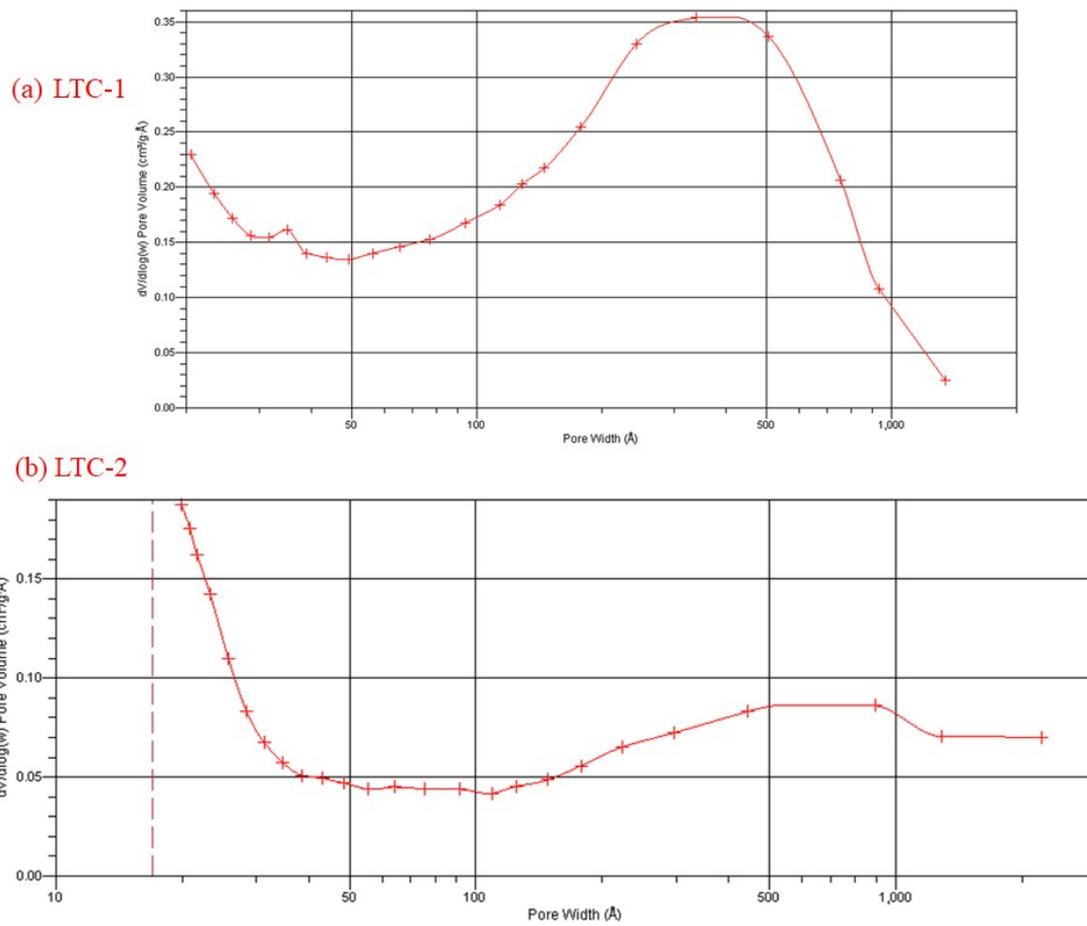


Fig. S6 BJH pore size distribution curves of (a) LTC-1 and (b) LTC-2.

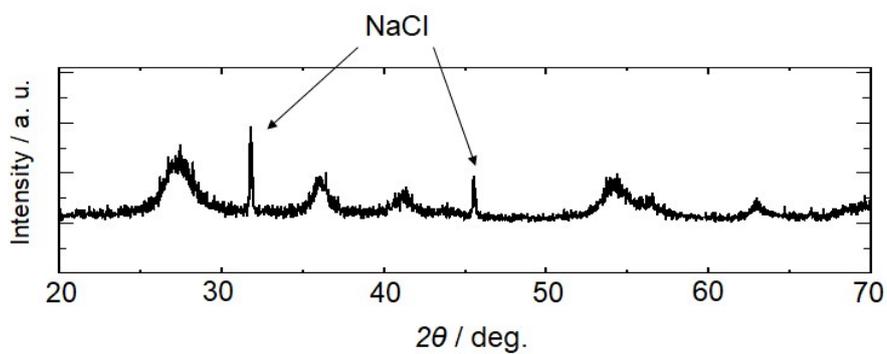


Fig. S7 Powder XRD pattern of TiO₂ particles (LTC-1) obtained before washing treatment with H₂O.

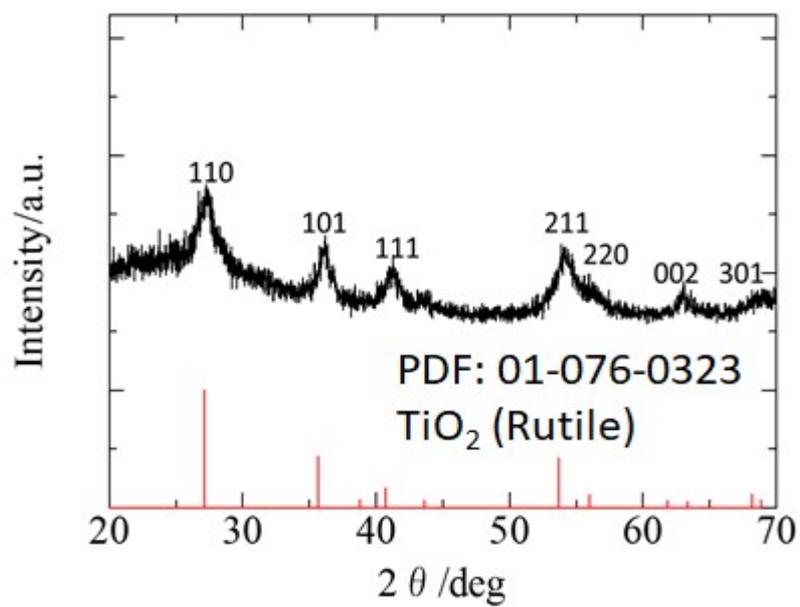


Fig. S8 Powder XRD pattern of TiO₂ particles (LTC-2) after washing treatment with H₂O.

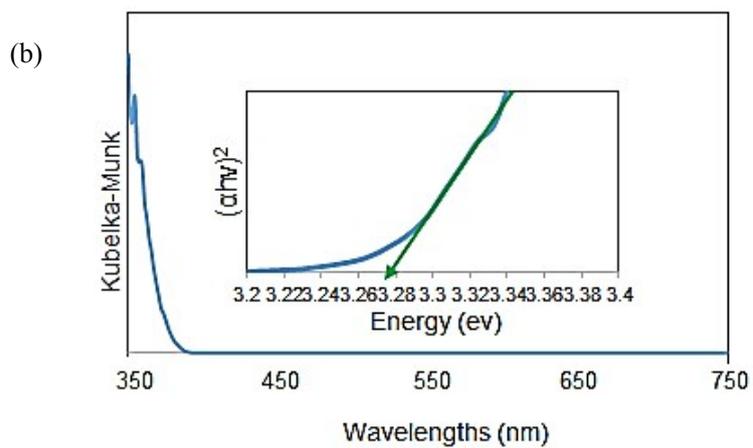
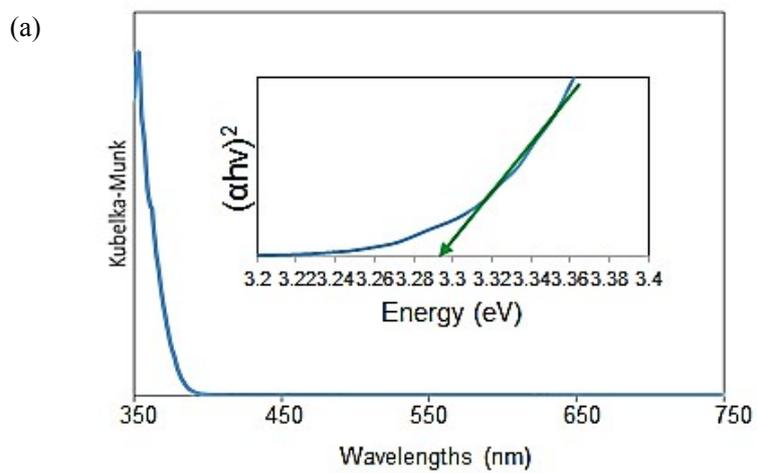


Fig. S9 Reflectance spectra of (a) LTC-1 and (b) LTC-2.

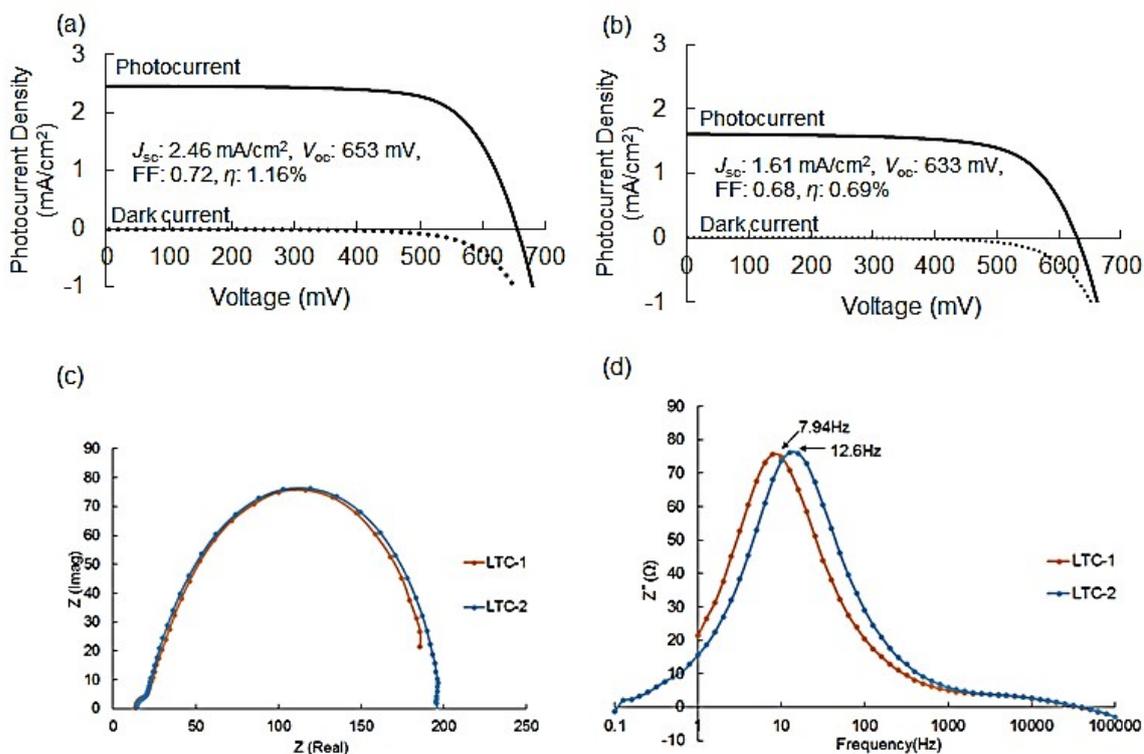


Fig. S10 Current density vs voltage curves of photoelectrochemical cells using TiO_2 films of (a) LTC-1 and (b) LTC-2, and electrochemical impedance spectra of the same devices, (c) Nyquist plots; (d) Bode phase plots.

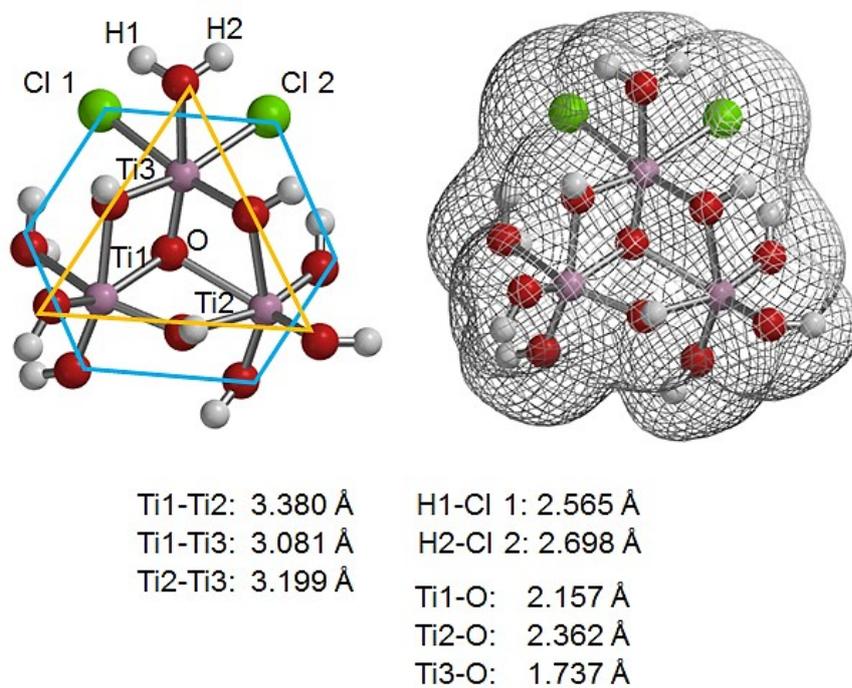


Fig. S11 A modelled trinuclear Ti(IV) cluster for another isomer. Each atom in the clusters is illustrated using pink for Ti(IV), green for Cl, red for O and white for H. Electron density is indicated as a silhouette. Selected bond distances are also presented.