Role of Water in the Transformation of Protonated Titanate Nanoribbons to Anatase Nanoribbons

Melita Sluban†‡ and Polona Umek†‡*

†Jožef Stefan Institute, Jamova cesta 39, SI-1000 Ljubljana, Slovenia
‡Jožef Stefan International Postgraduate School, Jamova cesta 39, SI-1000 Ljubljana, Slovenia

ABSTRACT: Transformation of layered protonated titanate (H$_2$Ti$_3$O$_7$) nanoribbons to anatase nanoribbons under hydrothermal conditions is a catalyzed process where topotactic transformation and dissolution–recrystallization compete. In the present work, the transformation was achieved with sufficiently high thermal input, calcination, or catalysis when performed under hydrothermal conditions. X-ray diffraction and scanning and transmission electron microscopy combined with crystallography of product materials revealed that the success of catalysis depended on the suspension’s pH value as well as on the counterions present in the reaction mixture. The process of the transformation from protonated titanate to anatase under hydrothermal conditions is explained for the reaction medium pH range of 1–13.7 with the aid of the ζ-potential of protonated titanate nanoribbons. Protonated titanate nanoribbons were stable under basic conditions, and their transformation to anatase nanoribbons depended on the counterions present in the reaction mixture and their concentration as well. With decreasing the pH of the reaction mixture, both processes—topotactic transformation and dissolution–recrystallization—were accelerated. Upon the hydrothermal transformation, the nanoribbons served as the substrate for the heterogeneous nucleation of anatase nanocrystals. Sodium titanate nanoribbons were found to be suitable for the transformation to anatase nanoribbons under hydrothermal conditions as well. Presence of water in the reaction mixture was revealed to be crucial for the transformation progress under hydrothermal/solvothermal conditions since used organic solvents served only as a thermal reaction medium and did not promote the catalytic transformation.

INTRODUCTION

Titanium dioxide (TiO$_2$) has been a subject of extensive research over the last decades due to its photoactivity. Since one-dimensional (1D) morphology is more beneficial than the zero-dimensional one when considering charge separation, charge transfer, and the defect amount present in the material, 1D protonated titanates are appealing TiO$_2$ precursors. The transformation of layered protonated titanate (H$_2$Ti$_3$O$_7$) to TiO$_2$-B and further to anatase has already been a subject of intense research. The transformation is a condensation described by the equation H$_2$Ti$_3$O$_7$ → 3TiO$_2$ + H$_2$O. Theoretically, condensations can be achieved either (i) by the energy input high enough to overcome the activation energy of the reaction or (ii) by lowering the activation energy, that is, by catalysis. The typical catalysts for condensations are acids and bases. In practice, the first way is performed with calcination of protonated titanate in air at 800°C or some other atmospheres whereas catalysis is performed in an aqueous medium under hydrothermal or even ambient conditions. Despite several investigations, some important questions remain unanswered: (i) How does protonated titanate behave under basic hydrothermal conditions and (ii) how do different bases influence the transformation? (iii) What is the exact role of water or other solvents in the reaction medium?

First, we will briefly describe significant reported results for two different transformation approaches: (i) calcination in air and (ii) hydrothermal treatment in aqueous media under neutral and acidic conditions. Calcination of 1D protonated titanates in air is the most common approach to transform them into TiO$_2$. H$_2$Ti$_3$O$_7$ nanoribbons (NRs) have poor thermal stability; during heating, dehydration of more tightly bound water occurs between 100 and 250°C while the first structural changes start already between 180 and 230°C. Qamar et al. proposed that the protons in the protonated titanates could serve as the acid catalyst for the condensation of −OH groups during the heat treatment leading to an earlier anatase formation. Temperatures at which all of those changes take place highly depend on the initial morphology of the protonated titanate. For example, protonated titanate nanotubes start to transform to anatase already at temperatures as low as 200°C whereas calcination above 500°C is necessary.

Received: August 29, 2019
Published: September 5, 2019
for the conversion of protonated titanate nanoribbons to anatase nanoribbons (NRs).6,16

The transformation from H₂Ti₃O₇ to TiO₂ in aqueous media can proceed through two main mechanisms: (i) topotactic reaction and/or (ii) dissolution−recrystallization. The topotactic reaction occurs during the transformation of H₂Ti₃O₇ to anatase due to their structural similarities (Figure 1). The reaction proceeds through condensation among TiOH entities and in situ structural rearrangement of TiO₆ octahedra.11−14,17 This transformation usually happens with morphology preservation under milder reaction conditions as (hydrothermal treatment in water13,18 or 0.05 M HNO₃(aq)14) when the dissolution of the protonated titanate does not prevail.

Under stronger reaction conditions, i.e., in more acidic medium (2.63 M HNO₃15,19)15,19 reaction mixture with pH values of 019⁰ and at higher reaction temperatures, protonated titanates dissolve and the material recrystallizes in a thermodynamically favored rutile structure.11,15,19 In this case, the product TiO₂ nanoparticles have a new, nonrelated morphology compared to the starting material.

Transformation from protonated titanate to TiO₂ under hydrothermal conditions led to the investigation of the room-temperature stability of protonated titanate suspensions at different pH values.15,20 Protonated titanate nanotubes (HTiNTs) proved to be stable under basic and neutral conditions, as their aging in 0.1 M NaOH and deionized water for 5 months evoked minimal morphological changes in the material.15 HTiNTs transformed to the mixture of anatase and rutile nanoparticles after being exposed to 0.1 M H₂SO₄ for 1 month, whereas aging for 2 months resulted in a complete conversion to rutile nanoparticles.15 The transformation of HTiNTs was much slower when 0.1 M HCl or HNO₃ was used instead of H₂SO₄.15 These results confirm that the

---

**Figure 1.** Schematic presentation of topotactic transformation from protonated titanate (H₂Ti₃O₇) to anatase.

**Table 1. Products’ Labels, Transformation Conditions, and Products’ Phase Composition**

| sample          | transformation environment | T (°C) | t (h) | ΔT/Δt (°C min⁻¹) | phase composition               |
|-----------------|----------------------------|--------|-------|------------------|---------------------------------|
| TO-400, ref 16  | static air                 | 400    | 6     | 1                | TiO₂-B                          |
| TO-580, ref 16  | static air                 | 580    | 6     | 1                | TiO₂-B + anatase                |
| TO-650, ref 16  | static air                 | 650    | 6     | 1                | anatase                         |
| CH-NaOH         | 0.5 M NaOH(aq)             | 160    | 24    | 4                | (NaH₂)₂TiO₂                      |
| CH-N₂           | 2.0 M NH₃(aq)              | 160    | 24    | 4                | (NH₄H₂)₂TiO₂                     |
| CH-N₂-RT        | 2.0 M NH₃(aq) RT³⁰         | 24     |       |                  | (NH₄H₂)₂TiO₂ + anatase           |
| CH-N₂-RT        | 1.0 M NH₃(aq)              | 160    | 24    | 4                | H₂Ti₃O₇ + anatase                |
| CH-N₂-RT        | 0.5 M NH₃(aq)              | 160    | 24    | 4                | anatase                         |
| CH-W₁₂₀, ref 16 | deionized water            | 120    | 10    | 4                | H₂Ti₃O₇                         |
| CH-W₁₄₀         | deionized water            | 140    | 10    | 4                | H₂Ti₃O₇ + anatase                |
| CH-W₁₆₀-5       | deionized water            | 160    | 5     | 4                | H₂Ti₃O₇ + anatase                |
| CH-W₁₆₀         | deionized water            | 160    | 10    | 4                | anatase                         |
| MW-W₅           | deionized water            | 200    | 1/12  | afap            | H₂Ti₃O₇                         |
| MW-W₁₀          | deionized water            | 200    | 1/6   | afap            | H₂Ti₃O₇                         |
| MW-W₂₀          | deionized water            | 200    | 1/3   | afap            | H₂Ti₃O₇                         |
| MW-W₃₀          | deionized water            | 200    | 1/2   | afap            | H₂Ti₃O₇ + anatase                |
| MW-W₆₀          | deionized water            | 200    | 1     | afap            | H₂Ti₃O₇ + anatase                |
| MW-W₉₀          | deionized water            | 200    | 3/2   | afap            | H₂Ti₃O₇ + anatase                |
| MW-W₁₂₀ ref 16  | deionized water            | 200    | 2     | afap            | anatase                         |
| CH-HCl          | 0.05 M HCl(aq)             | 160    | 5     | 4                | anatase                         |
| MW-H₂SO₄        | 0.05 M H₂SO₄(aq)           | 200    | 2     | afap            | anatase                         |
| MW-acetic       | 0.1 M acetic acid(aq)      | 200    | 2     | afap            | anatase                         |
| MW-citric       | 0.1 M citric acid(aq)      | 200    | 2     | afap            | anatase                         |
| CH-MeCN         | CH₃CN                      | 160    | 24    | 4                | H₂Ti₃O₇                         |
| CH-ButOH        | BuOH                       | 160    | 24    | 4                | H₂Ti₃O₇                         |
| CH-EtOH         | EtOH                       | 160    | 24    | 4                | H₂Ti₃O₇                         |
| CH-EtOH/H₂O⁴⁺   | EtOH/H₂O⁴⁺                 | 160    | 24    | 4                | anatase                         |
| CH-AcOH         | AcOH                       | 160    | 10    | 4                | H₂Ti₃O₇                         |

³⁰Room temperature. ⁴⁺As fast as possible.
protonated titanate is not stable under acidic conditions and that the dissolution rate of protonated titanate depends on the acid nature ($\text{H}_2\text{SO}_4 > \text{HNO}_3 \approx \text{HCl}$).

In this work, we investigated the transformation of protonated titanate nanoribbons (HTiNRs), with $\text{H}_3\text{Ti}_2\text{O}_5$ layered structure, to TiO$_2$ nanoribbons aiming at: (i) determining the role of the water in the transformation, (ii) understanding the behavior of HTiNRs under hydrothermal conditions over the whole pH range, and (iii) explaining the relationship between the product morphology and the reaction environment. Within this perspective, the transformation reactions of HTiNRs were conducted under various hydrothermal and solvothermal conditions in addition to calcination in static air. A detailed insight into the transformation process as well as in the product formation was ensured by $\zeta$-potential measurements of the protonated titanate nanoribbons and electronic microscopy combined with crystallography of the products. To optimize the synthesis procedure, sodium titanate nanoribbons ($\text{(Na,Ti)}_2\text{O}_5$), the parent material of the protonated titanate nanoribbons ($\text{H}_3\text{Ti}_2\text{O}_5$), were used as a precursor for a direct transformation to anatase.

### EXPERIMENTAL SECTION

#### Materials Synthesis. Preparation of Precursor $\text{H}_3\text{Ti}_2\text{O}_5$ Nanoribbons.
Protonated titanate nanoribbons (HTiNRs) were prepared from the parent sodium titanate nanoribbons (NaTiNRs) by an ion-exchange process. The detailed procedure is described in our previous paper.$^{16}$ In brief, approximately 4 g of NaTiNRs were suspended in 500 mL of 0.1 M $\text{CH}_3\text{COOH(aq)}$ and stirred for 1 h. If the material did not sediment naturally afterward, the suspension was centrifuged. With the same procedure, the material was additionally washed four times. Then, HTiNRs were washed with water a few times until the pH of the supernatant was approximately 5.5. After final rinsing with EtOH, the material was dried in air at 100 °C for 12 h.

#### Annealing in Static Air.
The detailed procedure is described in ref 16: In brief, 150 mg of HTiNRs was weighed in an alumina boat, placed into an oven, and heated to the target temperature (400, 580, or 650 °C). Samples were maintained at the selected temperatures for 6 h and cooled down to room temperature afterward.$^{16}$ Samples’ labels, reaction conditions, and phase compositions are listed in Table 1.

#### Solvothermal Treatment in an Autoclave.
HTiNRs (150 mg) were suspended in 36 mL of deionized water. The reaction was performed in a Teflon-lined autoclave (Berghof, BR25; filling volume, 90%). The suspension was stirred at 300 rpm and heated to 160 °C at a heating rate of 4 °C min$^{-1}$. After thermal treatment for the predetermined time, the suspension was left to cool down to room temperature. The product was isolated with repeated washing with water and centrifugation until the pH of the supernatant was 5–6 and finally rinsed with EtOH. The material was then dried in an oven at 100 °C for 12 h. Samples’ labels, reaction conditions, and phase compositions are listed in Table S1.

#### Hydrothermal Treatment of Sodium Titanate Nanoribbons (NaTiNRs).
NaTiNRs (150 mg) were suspended in 36 mL of deionized water. The reaction was performed in a Teflon-lined autoclave (Berghof, BR25; filling volume, 90%). The suspension was stirred at 300 rpm and heated to 160 °C at a heating rate of 4 °C min$^{-1}$. After thermal treatment for the predetermined time, the suspension was left to cool down to room temperature. The product was isolated with repeated washing with water and centrifugation until the pH of the supernatant was 5–6 and finally rinsed with EtOH. The material was then dried in an oven at 100 °C for 12 h. Samples’ labels, reaction conditions, and phase compositions are listed in Table S1.

#### Materials Characterization.
Identification of phase composition of the samples was determined from the powder X-ray diffraction (XRD) patterns measured using a D4 Endeavor, Bruker AXS diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å) and a Sol-X energy-dispersive detector. Diffactograms were measured in the 2θ angular range with a step size of 0.02° s$^{-1}$ and a collection time of 3 s.

The morphology of the samples was investigated using a field emission scanning electron microscope (SEM) (Jeol 7600F). For the SEM analysis, the samples were dispersed in water and a drop of dispersion was deposited on a polished Al sample holder. Prior to the SEM investigation, an ca. 3 nm thick carbon layer or a Au/Pd layer was deposited on the samples to reduce the charging effect. The crystallinity and size distribution of the samples were investigated with a transmission electron microscope (TEM) (Jeol 2100, 200 keV). Specimens for TEM analyses were dispersed ultrasonically in methanol, and a drop of the dispersion was deposited onto a lacey carbon film supported by a copper grid.

Sodium content was determined from energy-dispersive X-ray data (EDX) measured using a field emission scanning electron microscope (JEOL 7600F) equipped with an EDX spectrometer elemental analysis system. The samples were pressed into pellets and placed on a carbon tape on an Al sample holder. The holder with the samples was coated with a thin carbon layer prior to the analyses.

$\zeta$-Potential of HTiNRs was measured using a $\zeta$-potential analyzer Brookhaven Instruments Corporation Zeta PALS applying Smoluchowski theory. For the measurement, approximately 5 mg of HTiNRs was dispersed in 280 mL of 0.01 M NaCl(aq) and ultrasonicated for 2 min. Suspension’s pH for measuring material’s $\zeta$-potential in acidic pH region

DOI: 10.1021/acs.jpcc.9b08225
J. Phys. Chem. C 2019, 123, 23747–23757
was adjusted by adding 0.1 M HCl(aq) solution to the stirring suspension. For the measurements in the basic pH region, 0.1 M NaOH(aq) solution was used. For each ζ-potential measurement, the required amount of the stirring suspension was then transferred into instrument’s cuvette.

Fourier transform infrared (FTIR) spectra of selected samples were measured with a PerkinElmer Spectrum 400 Series spectrometer equipped with an universal attenuated total reflectance accessory.

## RESULTS AND DISCUSSION

### Transformations of H₂Ti₃O₇ Nanoribbons to TiO₂ Nanoribbons. Annealing in Air.

In short, we discuss the transformations of the protonated titanate nanoribbons (H₂Ti₃O₇ NRs, HTiNRs) conducted under the most commonly employed reaction conditions, that is, calcination in air. Upon heating up to 400 °C, the precursor HTiNRs, with H₂Ti₃O₇ layered structure, undergo a transformation accompanied by the formation of different intermediates finally yielding TiO₂-B (H₂Ti₃O₇ → H₂Ti₆O₁₃ → H₂Ti₂O₇ → TiO₂-B). As we reported in our previous paper, during calcination at 400 °C HTiNRs first transformed to TiO₂-B phase (ICDD card no. 35-0088, TO-400). The XRD peaks of TO-400 nanoribbons appear to be broad with low intensity indicating their poor crystallinity (Figure S1). With increasing temperature, anatase started to form (ICDD card no. 86-1157, TO-580) and it was the only phase obtained after calcination of HTiNRs at 650 °C (Figure S1).

Calcination in air did not affect the nanoribbon morphology of the product TiO₂ NRs, as can be seen from the SEM images of the samples (Figures S2a,c and 2a). However, upon this transformation, the TO-400 nanoribbons became mesoporous (Figure S2b,d), and pore diameter ranges from 2 to 10 nm, which is characteristic of less dense TiO₂-B phase. The formation of porosity is attributed to a mismatch of the unite cell parameters between H₂Ti₆O₁₃ and TiO₂-B. Finally, in the TO-650 sample, which is of pure anatase phase, the porosity vanished; the nanoribbons are elongated along the a-axis and have rounded edges due to partial sintering, as evidenced by high-resolution TEM (HRTEM) and fast Fourier transformation (FFT) analyses (Figure 2).

### Transformation under Hydrothermal Conditions.

To investigate the role of water in the transformation of HTiNRs to TiO₂ transformations under hydrothermal conditions with pH ranging from 1 to 13.7 were conducted.

**Basic Conditions—NaOH(aq).** HTiNRs were hydrothermally treated in 0.5 M NaOH(aq) at 160 °C for 24 h (Table 1). XRD analysis of the CH-NaOH sample revealed that instead of transformation of the protonated titanate to TiO₂ phase, a partial ion exchange of protons with Na⁺ ions took place (Figure S3). The sodium content increased from 0.1 wt % for HTiNRs to 0.7 wt % for the CH-NaOH sample, as determined with EDX analyses. SEM investigations (not shown) indicated that the isolated NRs were intact in comparison to the starting HTiNRs. The amount of intercalated Na⁺ ions was high enough to stabilize the interlayer structure and thus prevented the transformation.

**Basic Conditions—NH₃(aq).** When NH₃(aq) was used as a reaction medium, the transformation of H₂Ti₃O₇ to anatase occurred faster with decreasing ammonia concentration, as evidenced with XRD analyses (Figure 3). After the hydrothermal treatment of HTiNRs in a 2.0 M NH₃(aq) solution, no TiO₂ phase was detected. This indicates that the amount of intercalated NH₄⁺ ions was high enough to stabilize the interlayered structure as in the case of 0.5 M NaOH(aq). Although the transformation did not proceed, three changes in the XRD peak connected to the d-spacing (2θ ~ 11°) of titanate layers were observed (Figure S4a): after the hydrothermal treatment, (i) the peak shifted to lower angles (from 11.56 to 11.08°), (ii) its intensity decreased, and (iii) it became broader. The shift to lower 2θ value was expected due to difference in size between NH₄⁺ ion and proton. The decrease in the peak’s intensity and its broadening suggest that the stacking of the titanate sheets is poorer in CH-N₂ than in the parent HTiNRs. In addition, when HTiNRs were stirred in 2 M NH₃(aq) at room temperature for 24 h (CH-2N-RT), the peak intensity decreased (2θ ~ 11°) and shifted to higher angles (to 11.75°), indicating a contraction of the interlayer spacing. This can be attributed to a partial substitution of protons with NH₄⁺ ions accompanied with removal of the interlayered water. The contraction of titanate layers was also
observed in Na$_2$Ti$_3$O$_7$ when Na$^+$ ions were substituted with K$^+$ at room temperature$^{31,32}$ and was attributed to the hydration status of the cations.$^{33}$ From FTIR spectra, it is evident that at hydrothermal conditions at 160$^\circ$C, more NH$_4^+$ ions intercalated between titanate layers (CH-N2) and the amount of interlayered water decreased in comparison to CH-N2-RT (Figure S4b). In the 1700−1400 cm$^{-1}$ region in the FTIR spectrum of precursor HTiNRs, only one band is observed at 1645 cm$^{-1}$, which is assigned to stretching and bending vibrations of interlayer water molecules. On the contrary, in the spectra of CH-2N-RT and CH-2N, two bands are observed: (i) the first one at 1645 cm$^{-1}$ and (ii) the second one at 1440 cm$^{-1}$, which is assigned to the NH$_4^+$ deformation. The intensity of the second band increased with the increase of reaction temperature (from room temperature to 160$^\circ$C), while the intensity of the first band decreased.

With decreasing ammonia concentration to 1.0 M, anatase was the major phase obtained and it was the only phase in the product material when a 0.5 M NH$_3$(aq)$^{16}$ solution was employed. This shows that titanate NRs are stable under highly basic conditions as they did not transform to TiO$_2$. Hydrothermal treatment of HTiNRs in 0.5 M NaOH(aq) (CH-NaOH) did not result in any TiO$_2$ formation while that was the only phase obtained when 0.5 M NH$_3$(aq) was used as a reaction medium under otherwise identical reaction conditions.$^{16}$ This indicates the importance of the cations present in the reaction mixture and the pH of the reaction medium as well.

The nanoribbon morphology was preserved during the hydrothermal treatment of HTiNRs in NH$_3$(aq), as evidenced with SEM images (Figure 4). However, in contrast to the bare smooth HTiNRs, the product nanoribbons were covered with small crystals, whose amount increased with decreasing NH$_3$(aq) concentration. It may be assumed that at lower NH$_3$(aq) concentration, NH$_4^+$ cations evoked material's dissolution, which resulted in the recrystallization of small anatase crystal on the surface of the product TiO$_2$ NRs. When the concentration of NH$_4^+$ ions was increased, more NH$_4^+$ intercalated between titanate layers and thus stabilized the layered structure. Typical nanocrystal (Figure 4b) has well-defined facets and a shape of a highly truncated bipyramid. The truncated bipyramidal of anatase grew in the (001) direction and is surrounded by the facets corresponding to planes, whereas the truncated facet belongs to the planes of anatase.

**Neutral Conditions—Convective Heating in an Autoclave.** A complete transformation of HTiNRs to anatase NRs was achieved during the hydrothermal treatment of HTiNRs in deionized water$^{16}$ at 160$^\circ$C already in 10 h (Figure S5). At this point, we would only like to point out to the reduction of the reaction time from 24 h, when reaction was conducted in 0.5 M NH$_3$(aq), to 10 h, when the reaction medium was deionized water.

**Neutral Conditions—Microwave-Assisted Heating.** Microwave-assisted reactions are well known for higher effectiveness compared to the analogue reaction systems performed with classical convective heating. This is due to the in-core volumetric heating of the reaction mixture when the reactants or reagents directly interact with microwave irradiation.$^{34}$ Transformation of HTiNRs to anatase was therefore investigated also with the assistance of microwave (MW) irradiation. To precisely follow the transformation progress, the reactions were terminated after different reaction times (Table 1 and Figure S6). From the corresponding XRD patterns (Figure S6), it is evident that the collapse of the layered structure of protonated titanate (0−60 min) was followed by the direct formation of anatase without the formation of an intermediate TiO$_2$-B phase. This is in contrast to the results obtained with calcination of HTiNRs in air (Figure S1). Also, under hydrothermal conditions, the transformation from protonated titanate to anatase proceeded faster than with calcination.
whereas the major discrepancy from the shape of nanocrystals (Figure S7d). Solution of acetic acid are rather similar (Figure S7b,c), complete conversion of H$_2$Ti$_3$O$_7$ to anatase. That is two times (CH-Cl sample), the reaction time of 5 h already su.

nanoribbon morphology was the most a...and heating techniques (an autoclave and an MW reactor) preserved during the hydrothermal treatment, as evidenced from the SEM analysis (Figure 5a). Nanoribbons' surface is fissured and covered with small crystals. A closer view of a characteristic nanoparticle (Figure 5b) suggests that the nanoparticles grow from the top of the nanoribbon rather than being deposited on it. The particle has a trapezoidal shape that can also be described as a truncated pyramid. FFT analysis and the dihedral angle measurement between the marked facets revealed that the truncated pyramid of anatase grows in the (001) direction, its lateral facets belong to the planes, and the truncated facet is attributed to the planes.

Acidic Conditions. Finally, the transformation of HTiNRs was conducted also under hydrothermal acidic conditions. For this, different acids (HCl, H$_2$SO$_4$, acetic acid, and citric acid) and heating techniques (an autoclave and an MW reactor) were used (Table 1).

XRD analyses of the samples confirmed that they all transformed to anatase phase under the selected reaction conditions. When the reaction was performed in an autoclave (CH-Cl sample), the reaction time of 5 h already sufficed for a complete conversion of H$_2$Ti$_3$O$_7$ to anatase. That is two times faster in comparison to the transformation, conducted in pure water (CH-W160, Table 1).

SEM analyses of the samples revealed that they all consisted of nanoribbons that were covered with nanocrystals, whose shape depends on the acid type used in the reaction (Figure S7). When the reaction was performed in HCl(aq), the nanoribbon morphology was the most affected. This can be due to longer reaction time (5 h) compared to reaction times of other reaction systems (2 h). Products obtained after hydrothermal treatment in H$_2$SO$_4$(aq) and the aqueous solution of acetic acid are rather similar (Figure S7b,c), whereas the major discrepancy from the shape of nanocrystals covering the nanoribbons' surface was obtained after employing the aqueous solution of citric acid as a reaction medium (Figure S7d).

TEM analyses of the MW-acetic and MW-citric samples provided a deeper insight into the role of counterions during the transformation from H$_2$Ti$_3$O$_7$ to anatase. The transformation in aqueous 0.1 M acetic acid solution resulted in the growth of truncated pyramidal nanoribbons (Figure 6a). The selected truncated pyramid grows in the (001) direction is surrounded by the (101) planes and truncated with a facet belonging to the (001) planes, as determined by FFT. In addition, the identity between FFT patterns taken from the nanocrystal (1) and the nanoribbon (2) regions suggests that the nanocrystal epitaxially grew from the nanoribbons’ surface, which functioned as a substrate.

The appearance of the MW-citric nanoribbons differs the most from the products obtained with other acids (Figure 6). However, the nanoribbons of the MW-citric sample are covered with higher amount of smaller nanoparticles that often do not have well-developed facets compared to the nanocrystals of the other samples. Nanocrystals covering the NRs surface of MW-citric sample were pyramidal (Figure 6b). Due to a large number of nanoparticles on individual nanoribbons, the HRTEM analysis was difficult. The measured interplanar distance between the planes that are parallel to the pyramid’s lateral facet belongs to the anatase planes (inset of Figure 6b). The measured angles between the opposite circumferential planes of the pyramidal particles vary from approximately 40° to 55°. The theoretical angle between the opposite circumferential planes of the anatase pyramid is 43.4°. Even though the measured dihedral angle of some particles was around 44°, the variation in angle value appears most probably due to the non-fully-developed particle’s facets.

The difference in the appearance of nanocrystals covering nanoribbons arises from the shape- and size-tailoring role of the counterions present in the reaction media. Cl$^-$, CH$_3$COO$^-$, and SO$_4^{2-}$ anions are smaller than the citrate anion, which is also the only tridentate adsorbate among them. Cl$^-$ and SO$_4^{2-}$ anions are reported to preferentially adsorb on anatase planes.

Lowering the surface energy of the planes would additionally promote the growth of the truncated facet leading to the pyramidal shape of the particles. Since the pyramidal shape of the particles was obtained only after the employment of citric acid, the plausible explanation could be that citrate anions stabilize the anatase planes even better than other anions. Since the citrate anion is a tridentate adsorbent, one anion could adsorb also on the neighboring facets limiting the particle growth and affecting its size. This could explain the smaller size of nanoparticles covering the nanoribbons’ surface compared to the samples prepared in other acidic reaction media as well.

Solvothermal Conditions—Convective Heating in an Autoclave. To fully understand the role of water in the transformation of H$_2$Ti$_3$O$_7$ to TiO$_2$, experiments in organic liquids were conducted as well. Table 1 summarizes the
reaction conditions. When the reaction was performed in a polar aprotic solvent (MeCN), no protonated titanate transformed to TiO$_2$, as evidenced by the XRD analysis (Figure S8a). The use of a protic solvent (BuOH) did not improve the transformation progress, and in the same way, an increase in polarity of the solvent (EtOH) did not result in any TiO$_2$ formation either (Figure S8). Finally, the addition of water to EtOH as a solvent (25 vol %) led to the complete transformation of protonated titanate to anatase (Figure S8b).

In addition, when pure acetic acid was used as a reaction medium, no transformation occurred.

SEM analyses of the products revealed that when protonated titanate did not transform to TiO$_2$, no morphological or surface changes of NRs occurred (Figure S9a). Those NRs appeared identical to the nanoribbons in the starting material (HTiNRs). When water was added to the reaction medium, the product anatase NRs had a typical appearance of the hydrothermally transformed anatase NRs—the nanoribbon’s surface was covered with small nanocrystals (Figure S9b).

The reduction of the reaction temperature from 580 °C for annealing in air to 160 °C for the hydrothermal treatment is attributed to the catalytic role of the water and the species derived from it (H$^+$). These results suggest that when the reaction is performed in an organic solvent, the latter cannot donate protons to catalyze the condensation reaction. A similar observation was made by Yin et al.\textsuperscript{18} by hydrothermal treatment of H$_2$Ti$_4$O$_9$·0.25H$_2$O in pure EtOH, first, structural changes were observed above 200 °C, and the transformation was not completed at 325 °C. Therefore, the solvent acts only as a thermal medium, where heating at 160 °C does not suffice for the transformation of protonated titanate to anatase.

Transformations of (Na,H)$_2$Ti$_3$O$_7$ Nanoribbons to TiO$_2$ Nanoribbons. Neutral Conditions—Convective Heating in an Autoclave. To increase the process effectiveness of the transformation from titanate to anatase, also sodium titanate nanoribbons ((Na,H)$_2$Ti$_3$O$_7$, NaTiNRs) were used as a starting material for a one-pot transformation to TiO$_2$ (Table S1).

Even though anatase was the major phase, obtained after 10 h of the hydrothermal treatment in deionized water at 160 °C, the reaction time of 24 h was required for a complete transformation (Figure S10).

The sample obtained after the reaction time of 10 h was composed of nanoribbons that were covered with (truncated) pyramidal crystals growing from the nanoribbon’s surface (Figure 7a), resembling thorns on the rose stem. With prolonged reaction time, the amount of nanocrystals increased at the expense of nanoribbons (Figure 7b). The particle grows in the (001) direction and is enclosed with facets belonging to the planes (c and d).

Hydroxyl anions are assumed to preferentially adsorb onto facets thus lowering their growth rate.\textsuperscript{37} In addition, also cations can tailor the nanoparticle’s shape through preferential adsorption, where the cation’s size and charge density play an important role.\textsuperscript{38} On anatase facets, O$^{2-}$ are present on the surface of {100} planes, but slightly beneath the layers of {001} planes. Li$^+$ ions were reported to be able to successfully adsorb on {100} and {001} planes, whereas larger K$^+$ with smaller charge density could adsorb only on {100} planes.\textsuperscript{38} Na$^+$ ion with size between Li$^+$ and K$^+$, when considering their ionic size and charge density, could probably adsorb on O$^{2-}$ sites of both planes; however, the adsorption on {100} planes would be easier. Therefore, the combination of retaining the crystal growth in ⟨101⟩ (Na$^+$) and ⟨100⟩ (OH$^-$) directions would result in particles with predominating ⟨001⟩ facets, as evidenced in the CH-NaTiNRs10 sample.

HTiNRs ζ-Potential and Behavior in Aqueous Media. Now, let us rationalize the results of the hydrothermal
treatment of HTiNRs under different hydrothermal conditions. The in situ transformation from $\text{H}_2\text{Ti}_3\text{O}_7$ to anatase is a condensation, which can be theoretically catalyzed with either bases or acids. The experimental results revealed that the transformation proceeded under a wide pH range of the reaction medium ($1 \text{ (0.1 M HCl(aq))–11.5 (0.5 M NH}_3\text{(aq))}$).

When trying to understand the behavior of HTiNRs in different reaction media, their $\zeta$-potential can be of a considerable help. Figure 8 shows the dependence of HTiNRs $\zeta$-potential on the suspension’s pH. The graph is divided into three regions: (i) region I where the suspension is acidic ($\text{pH < 3.5}$) and HTiNRs have a positive $\zeta$-potential, (ii) region II with still acidic and neutral suspension ($3.5 \leq \text{pH} \leq 7$) and a negative $\zeta$-potential of HTiNRs, and (iii) region III where the suspension is basic ($\text{pH > 7}$) and HTiNRs have a negative $\zeta$-potential as well.

We will start with the explanation of HTiNRs behavior in region III ($\text{pH > 7}$, HTiNRs have a negative $\zeta$-potential). Sodium titanates ($\text{(Na,H)}_2\text{Ti}_3\text{O}_7$) are formed in highly concentrated alkaline medium ($10 \text{ M NaOH(aq)}$) and are therefore stable under highly basic conditions ($\text{pH > 12}$). Under those conditions, the HTiNRs surface is negatively charged and repelled from the HTiNRs surface. Cations from the reaction medium (Na$^+$ ions or NH$_4^+$ ions) exchange protons at the surface of the nanoribbons and between the titanate layers and thus stabilized the layered structure yielding (Na$_2$,H)$_2$Ti$_3$O$_7$ or (NH$_4$,H)$_2$Ti$_3$O$_7$.

With lowering the NH$_3$(aq) concentration in the reaction medium, the cation’s role of the base and the pH of the reaction mixture become significant. While HTiNRs did not transform to anatase when exposed to 0.5 M NaOH(aq) ($\text{pH > 13}$, CH-NaOH) and 2 M NH$_3$(aq) ($\text{pH \sim 11.8, CH-N2}$) (Figures 3 and S3), the HTiNRs completely transformed to anatase NRs when hydrothermally treated in 0.5 M ammonia solution ($\text{pH \sim 11.5, CH-N0.5}$) under otherwise identical reaction conditions (CH-NaOH). Under these conditions, most likely two processes took place: (i) topochemical transformation of titanate to anatase NRs since the morphology was retained and (ii) NH$_4^+$ ions from the reaction mixture exchanged protons at the surface of HTiNRs and caused partial dissolution of the material, which resulted in the deposition of TiO$_2$ nanocrystals at the surface of the TiO$_2$ NRs (Figure 4). In this case the amount of NH$_4^+$ ions was too low to stabilize the layered titanate structure. Zhao et al. reported that hydrothermal treatment of tetrabutyl titanate in 0.1 M NaOH at 180 °C ($\text{pH = 13}$) favors the formation of brookite phase, and with increasing NaOH concentration up to 0.5 M, the amount of brookite phase decreases on behalf of Na$_2$Ti$_2$O$_5$.

Under neutral and slightly acidic conditions ($3.5 \leq \text{pH} \leq 7$, region II in Figure 8), HTiNRs have a negative $\zeta$-potential due to their weak acidic nature. pH of deionized water, used in the reactions, was 5.5 due to dissolved CO$_2$ from air. Therefore, when the transformation of HTiNRs was hydrothermally performed in water, the material’s surface was negatively charged and attracted H$_3$O$^+$ from the reaction medium. Therefore protons could interact with the surface of HTiNRs and penetrate between the titanate layers to catalyze the condensation from protonated titanate to anatase.

With decreasing pH of the reaction medium ($\text{pH < 3.5}$, region I in Figure 8), the HTiNRs surface became positively charged. Nevertheless, when aqueous 0.1 M acidic solutions were used as reaction media, the transformation to anatase NRs proceeded faster than in deionized water. From SEM analyses of the samples, it is obvious that material’s dissolution was also promoted. Protons from the reaction medium have therefore two functions: (i) they catalyze the condensation reaction and (ii) destabilize the titanate structure leading to its dissolution. When aqueous 0.1 M acidic solutions were used as reaction media, it seems that protons did not have a sufficiently high enough chemical potential to completely dissolve the material before it would transform to anatase. Maybe under those reaction conditions the acid anions (like Cl$^-$, CH$_3$COO$^-$) also succeeded to sufficiently stabilize the titanate surface against dissolution.

It is reported that with increasing acid concentration in the reaction medium (e.g., for HNO$_3$, $c \geq 2.65 \text{ M}$), the dissolution of the material excels over a topotactic reaction. Surface of HTiNRs is highly protonated, which destabilizes the crystal structure, leading to leaching of the surface TiO$_6$ octahedra and material dissolution. Finally, material recrystallizes in a thermodynamically favored rutile phase with normally a new, to precursor nonrelated, morphology.

Let us now consider the morphology of anatase samples synthesized under various hydrothermal conditions. All of the anatase samples were composed of nanoribbons covered with nanocrystals. The amount of nanocrystals covering NRs strongly depended on the reaction medium as the solubility of protonated titanate increases with decreasing pH of an aqueous suspension and also varies with the acid type. Furthermore, the shape of nanocrystals covering the nanoribbons depended on the reaction medium as well. Nanocrystals, produced under 0.5 M NH$_3$(aq) appeared more rectangular, whereas those obtained under neutral conditions were more trapezoidal. Finally, under acidic conditions, pyramidal particles were obtained too (MW-citrice). However, a more detailed HRTEM investigation revealed that those particles are closely related as: (i) they all have a differently truncated (bi)pyramidal shape, (ii) they grow in the ⟨001⟩ direction, and (iii) their lateral facets belong to the {110} planes and the truncated one to the {001} planes. This rather small morphology variety of nanocrystals, when considering the numerous different reaction conditions employed, can be due to the templated growth of nanoparticles. Heterogeneous nucleation requires less energy than the homogeneous one, and protonated titanate or anatase nanoribbons served...
excellently as a substrate on which nanocrystals grew. The observation of epitaxial growth was supported also with HRTEM investigations (Figure 6a). Counterions influenced mainly the solubility of protonated titanate and, consequently, the number and size of the grown crystals. However, in the case of the MW-citric sample, citrate anions had the major influence on the appearance of nanocrystals—they were smaller in comparison to other obtained samples and with finished pyramidal shape, which is most probably due to the tridentate ability of citrate anions.

When NaTiNRs were used as a precursor for a TiO₂ synthesis, they could not transform directly to anatase due to the presence of Na⁺ ions. Therefore, the ion-exchange process took place first and then topotactic transformation from protonated titanate to anatase occurred, and/or sodium titanate was dissolved and anatase nanocrystals were recrystallized from the solution. SEM investigation suggests that both processes took place. However, since the in situ transformation from NaTiNRs to TiO₂ NRs is slower than the transformation from HTiNRs to TiO₂ due to the additional ion-exchange step, more material dissolved. Then, counterions influenced the crystal growth through preferential adsorption on specific anatase planes.

Finally, transformation progress from HTiNRs to TiO₂ NRs under solvothermal conditions appeared more similar to the processes induced by calcination than hydrothermal treatment. Organic solvents did not ensure species that could catalyze the condensation in protonated titanate and seem to serve only as a thermal medium.

**CONCLUSIONS**

The transformation of protonated titanate nanoribbons to anatase nanoribbons was conducted under numerous hydrothermal conditions varying the medium’s pH from 1 to 13.7 and its ionic composition. During the transformation, two processes compete—topotactic transformation and dissolution-recrystallization—where both of them were affected by the reaction medium’s pH value, as explained with HTiNRs ζ-potential, and the presence of counterions. Even though HTiNRs (H₂TiO₃ NRs) are nominally stable under basic conditions, they can be transformed to anatase NRs if the right base and pH are chosen. HTiNRs were successfully transformed in 0.5 M NH₃(aq) under hydrothermal conditions where two processes took place: (i) topochemical transformation of titanate NRs to anatase NRs and (ii) NH₄⁺ cations from the reaction mixture exchanged protons at the surface of HTiNRs and caused partial dissolution of the material, which resulted in the deposition of TiO₂ nanocrystals at the surface of TiO₂ NRs. With increasing acidity of the reaction medium (pH value down to 1), the transformation proceeded faster due to the proton catalysis. The product materials were anatase nanoribbons covered with smaller anatase nanocrystals. There, nanoribbon structure was preserved due to the topotactic transformation and served as a substrate for the subsequent nanoparticle’s growth, which was additionally tailored with counterions present in the reaction medium. Water revealed to be crucial for the successful transformation of protonated titanate NRs to anatase NRs, while solvothermal treatment of HTiNRs in organic liquids did not result in any TiO₂ phase formation. When the reaction medium cannot donate species to catalyze the transformation, it acts only as a thermal medium and the reaction temperature of 160 °C did not suffice for the material’s transformation. Finally, an one-pot transformation of sodium titanate nanoribbons, a parent material of HTiNRs, to anatase NRs under hydrothermal conditions was achieved. There, the dissolution-recrystallization process was pronounced due to the additional intermediate ion-exchange step.

**REFERENCES**

(1) Carp, O.; Huisman, C. L.; Reller, A. Photoinduced reactivity of titanium dioxide. *Prog. Solid State Chem.* 2004, 32, 33–177.
anatase under hydrothermal treatment. Transition of lepidocrocite-type protonated layered titanates into nanofibers covered with anatase nanocrystals: a delicate structure and thermal stability of titanate nanotubes. Nanotechnology 2006, 17, 5922–5929.

6) Kitakittipong, K.; Scott, J.; Amal, R. Hydrothermally synthesized titanate nanostructures: Impact of heat treatment on particle characteristics and photocatalytic properties. ACS Appl. Mater. Interfaces 2011, 3, 3988–3996.

7) Zhang, M.; Jin, Z.; Zhang, J.; Guo, X.; Yang, J.; Li, W.; Wang, X.; Zhang, Z. Effect of annealing temperature on morphology, structure and photocatalytic behavior of nanohedral H₂Ti₃O₇(OH)₉. J. Mol. Catal. A 2004, 217, 203–210.

8) Wang, Y.; Feng, C.; Zhang, M.; Yang, J.; Zhang, Z. Visible light active N-doped TiO₂ prepared from different precursors: Origin of the visible light absorption and photocactivity. Appl. Catal., B 2011, 104, 268–274.

9) Wang, G.; Wang, H.; Ling, Y.; Tang, Y.; Yang, X.; Fitzmorris, R. C.; Wang, C.; Zhang, J. Z.; Li, Y. Hydrogen-treated TiO₂ nanowire arrays for photoelectrochemical water splitting. Nano Lett. 2011, 11, 3026–3033.

10) Tang, X.; Li, D. Sulfur-doped highly ordered TiO₂ nanotubular arrays with visible light response. J. Phys. Chem. C 2008, 112, 5405–5409.

11) Zhu, H. Y.; Lan, Y.; Gao, X. P.; Ringer, S. P.; Zheng, Z. F.; Song, D. Y.; Zhao, J. C. Phase transition between nanostructures of titanate and titanium dioxides via simple wet-chemical reactions. J. Am. Chem. Soc. 2005, 127, 6730–6736.

12) Yu, H.; Yu, J.; Cheng, B.; Zhou, M. Effects of hydrothermal post-treatment on microstructures and morphology of titanate nanoribbons. J. Solid State Chem. 2006, 179, 349–354.

13) Mao, Y.; Wong, S. S. Size- and shape-dependent transformation of nanosized titanate into analogous anatase titanita nanostructures. J. Am. Chem. Soc. 2006, 128, 8217–8226.

14) Zhu, G.; Lan, Y.; Song, D. J.; Xi, Y.; Zhao, J. et al. Hydrogen titanate nanofibers covered with anatase nanocrystals: a delicate structure achieved by the wet chemistry reaction of the titanate nanofibers. J. Am. Chem. Soc. 2004, 126, 8380–8381.

15) Bavykin, D. V.; Friedlich, J. M.; Lapkin, A. A.; Walsh, F. C. Stability of aqueous suspensions of titanate nanotubes. Chem. Mater. 2006, 18, 1124–1129.

16) Rutar, M.; Rozman, N.; Pregelj, M.; Koros, B.; Dominko, R.; Arcin, D. Effect of alkali metal ion assisted synthesis of colloid inorganic nanocrystals: Application to the microanatase octahedron. CrystEngComm 2009, 11, 4252–4257.

17) Yuan, H.; Besselink, R.; Liao, Z.; Ten Elshof, J. E. The swelling behavior of lepidocrocite-type protonated layered titanates into anatase under hydrothermal treatment. Sci. Rep. 2015, 5, No. 4584.

18) Yin, S.; Uchida, S.; Fujiyomo, M.; Sato, T. Phase transformation of protonic layered tetratitanate under solvothermal conditions. J. Mater. Chem. 2019, 9, 1191–1195.

19) Yu, Y.; Zhai, D. Single-crystalline TiO₂ nanorods: Highly active and easily recycled photocatalysts. Appl. Catal., B 2007, 73, 166–171.

20) Marinkovic, B. A.; Fredholm, Y. C.; Morgado, E.; J.; Jardim, P. M.; Rizzo, F. Structural resistance of chemically modified 1-D nanostuctured titanates in inorganic acid environment. Mater. Charact. 2010, 61, 1009–1017.

21) Umek, P.; Korosec, R. C.; Jančar, B.; Dominko, R.; Arcin, D. The influence of the reaction temperature on the morphology of sodium titanate 1 D nanostructures and their thermal stability. J. Nanosci. Nanotechnol. 2007, 7, 3502–3508.

22) Feist, T. P.; Davies, P. K. The soft chemical synthesis of TiO₂ (B) from layered titanates. J. Solid State Chem. 1992, 101, 275–295.

23) Akimoto, I.; Chiba, K.; Kimura, N.; Hayakawa, H.; Hayashi, S.; Gotoh, Y.; Iedamoto, Y. Soft-chemical synthesis and electrochemical property of H₂Ti₁₂O₃₅ as a negative electrode material for rechargeable lithium-ion batteries. J. Electrochem. Soc. 2011, 158, A546–A549.

24) Zhu, G.-N.; Wang, C.-X.; Xia, Y.-Y. Structural transformation of layered hydrogen trititanate (H₃Ti₃O₇) to TiO₂(B) and its electrochemical profile for lithium-ion intercalation. J. Power Sources 2011, 196, 2848–2853.

25) Morigao, E.; J.; Jardim, P. M.; Marinkovic, B. A.; Rizzo, F. C.; De Abreu, M. A. S.; Zlatin, J. L.; Araújo, A. S. Multistep structural transition of hydrogen trititanate nanotubes into TiO₂-B nanotubes: A comparison study between nanostructured and bulk materials. Nanotechnology 2007, 18, No. 495710.

26) Tournoux, M.; Marchand, R.; Brohan, L. Layered K₂TiO₃ and the open metastable TiO₂(B) structure. Prog. Solid State Chem. 1986, 17, 33–52.

27) Umek, P.; Bittencourt, C.; Guttmann, P.; Gletsner, A.; Škapan, S. D.; Arčon, D. Mn⁴⁺ substitutional doping of TiO₂ nanoribbons: A three-step approach. J. Phys. Chem. C 2011, 115, 21250–21257.

28) Kasatoška, K.; Akimoto, J. Soft chemical synthesis and crystal structure of novel hydrogen titanium oxide H₂Ti₁₂O₃₅. J. Ceram. Soc. Jpn. 2016, 124, 710–713.

29) Zhao, B.; Lin, L.; He, D. Phase and morphological transitions of titanate/titanita nanostructures from an anatase to an alkali hydrothermal environment. J. Mater. Chem. A 2013, 1, 1659–1668.

30) Dias, A. J.; Lima, S.; Carriazo, D.; Rives, V.; Pillinger, M.; Valente, A. A. Exfoliated titanate, niobate and titanoborate nanosheets as solid acid catalysts for the liquid-phase dehydration of d-xylene into furfural. J. Catal. 2006, 244, 230–237.

31) Li, N.; Zhang, L.; Chen, Y.; Fang, M.; Zhang, J.; Wang, H. Highly efficient, irreversible and selective ion exchange property of layered titanate nanostructures. Adv. Funct. Mater. 2012, 22, 835–841.

32) Viana, B. C.; Ferreira, O. P.; Filho, A. G. S.; Hidalgo, A. A.; Filho, J. M.; Alves, O. L. Alkaline metal intercalated titanate nanotubes: A vibrational spectroscopy study. Vib. Spectrosc. 2011, 55, 183–187.

33) Petit, S.; Righi, D.; Madejova, J.; Decarreau, A. Interpretation of the infrared NH₄⁺-clay spectrum of the NH₄⁺-clay: Application to the evaluation of the layer charge. Clay Miner. 1999, 34, 543–549.

34) Baghbanzadeh, M.; Carbone, L.; Cozzoli, P. D.; Kappe, C. O. Microwave-assisted synthesis of colloidal inorganic nanocrystals. Angew. Chem., Int. Ed. 2011, 50, 11312–11359.

35) Wu, L.; Yang, B. X.; Yang, X. H.; Chen, G. Z.; Li, Z.; Zhao, H. J.; Gong, X. Q.; Yang, H. G. On the synergistic effect of hydrohalic acids in the shape-controlled synthesis of anatase TiO₂ single crystals. CrystEngComm 2013, 15, 3252–3255.

36) Hisosono, E.; Fujibara, S.; Imai, H.; Honma, J.; Masaki, I.; Zhou, H. One-step synthesis of nano–micro chestnut TiO₂ with rutile microfiber on the nanocrystal octahedron. ACS Nano 2007, 1, 273–278.

37) Pan, J.; Wu, X.; Wang, L.; Liu, G.; Lu, G. Q.; Cheng, H.-M. Synthesis of anatase TiO₂ rods with dominant reactive (010) facets for the photocatalysis of CO₂ to CH₄ and use in dye-sensitized solar cells. Chem. Commun. 2011, 47, 8361–8363.

38) Yang, M.-H.; Chen, P.-C.; Tsai, M.-C.; Chen, T.-T.; Chang, I. C.; Chiu, H.-T.; Lee, C.-Y. Alkaline metal ion assisted synthesis of faceted anatase TiO₂. CrystEngComm 2015, 13, 2966–2971.

39) Shannon, R. D.; Prewitt, C. T. Effective ionic radii in oxides and fluorides. Acta Crystallogr., Sect. B: Struct. Sci. 1969, 25, 925–946.

40) Izawa, H.; Kikkawa, S.; Koizumi, M. Cation exchange selectivity for layered titanates, H₂Ti₃O₇. J. Solid State Chem. 1985, 60, 264–267.

41) Chen, C.; Xu, L.; Sewandi, G. A.; Kusunose, T.; Tanaka, Y.; Nakanishi, S.; Feng, Q. Microwave-assisted topochemical conversion...
of layered titanate nanosheets to \{010\}-faceted anatase nanocrystals for high performance photocatalysts and dye-sensitized solar cells. 

*Cryst. Growth Des.* **2014**, *14*, 5801−5811.

(42) Pu, Y.; Chen, Q.; Sun, Z.; Rodriguez, P.; Huang, L. Anomalous phase transition of layered lepidocrocite titania Nanosheets to anatase and rutile. *Cryst. Growth Des.* **2019**, *19*, 3298−3304.