

Synthesis and characterization of hydrothermally grown potassium titanate nanowires

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Potassium titanate (KT) nanowires were synthesized by a one-step hydrothermal reaction between TiO_2 and aqueous KOH solution. The effects of KOH concentration and reaction time on hydrothermal formation and KT nanowire growth were investigated. The nanowire growth mechanism was elucidated using a combined study of powder X-ray diffraction, and scanning and transmission electron microscopy. The results revealed that hydrothermal growth was initiated by the formation of amorphous-like Ti-O-K sheets in anatase. Increasing hydrothermal reaction time caused the transformation of anatase to Ti-O-K sheets, from which potassium hexa-titanate ($\text{K}_2\text{Ti}_6\text{O}_{13}$) nuclei formed and grew to establish one-dimensional morphology through preferential growth along the b-axis. It was revealed that the hydrothermal reactions followed a quite different mechanism than the well-known calcination route. Potassium tetra-titanate ($\text{K}_2\text{Ti}_4\text{O}_9$) crystals formed in the amorphous region using the hexa-titanate phase as a nucleation site for heterogeneous crystallization. Increasing the KOH concentration in the solution accelerated the hydrothermal reaction rate.

Key words: Potassium titanate, Hydrothermal, High-resolution transmittance electron microscopy (HRTEM).

Introduction

Potassium titanates (KT , $\text{K}_2\text{O} \cdot n\text{TiO}_2$, $n = 2, 4, 6, 8$), a wide family of artificial crystals with different morphologies (whiskers, nanowires), are of great interest owing to their tunnel- or layered-type crystalline structures [1, 2]. Among them, layered potassium tetra-titanates ($\text{K}_2\text{Ti}_4\text{O}_9$, $n=4$) have specific photoluminescence and photovoltaic activity that makes them good candidate materials for H_2 evolution via the water cleavage reaction even without using co-catalysts [3]. In addition, tunneled potassium hexa-titanates ($\text{K}_2\text{Ti}_6\text{O}_{13}$, $n=6$) are widely used as reinforcing agents in composites to improve the mechanical performance of metals, ceramics, and plastics [4-6]. Recent studies have shown that it is possible to produce mixtures of potassium tetra/hexa-titanates at once in a sol-gel reaction [6, 7]. They can preserve their photocatalytic activity in polymer matrices, and the final photo-responsive properties are highly dependent on the size and morphology, which is controlled by the change in Ti/K ratio of the precursors. Owing to their good photo-responsive properties, chemical and thermal stability, superior surface area provided by their high aspect ratio, and high mechanical properties at low cost, potassium tetra- and hexa-titanate whiskers and fibers have been used widely in functional and structural applications [8, 9].

Many researchers have studied the formation and growth of potassium titanate products with different

morphology and chemistry through a variety of methods including sol-gel [10, 11] calcination [12-14], flux growth [15, 16], and hydrothermal [17-19]. The calcination method is used commercially to produce short fibers or whiskers with broad size distribution. Better-controlled methods are needed to acquire products at the nano scale. Hydrothermal growth is a one-step, environmentally friendly, and inexpensive method in which the morphology, size, and purity of the product can be controlled under moderate conditions. In addition, it is possible to gain high production efficiency in the formation of nanosized particles or nanowires [20, 21].

In the production of KT structures by the hydrothermal method, KOH is commonly used as the potassium source, but a variety of titanium sources such as hydrated titania [18], Ti-alkoxides [22], titanium metal [23], anatase [24], and an anatase-rutile mixture [2] could be used at considerably lower temperatures under supercritical or subcritical conditions. Wang *et al.* [3] reported the use of hydrated TiO_2 as the Ti precursor; in this case, $\text{K}_2\text{Ti}_6\text{O}_{13}$ formation was observed only when the hydrothermal temperature and the KOH concentration were high. They stated that using highly reactive precursors such as hydrated TiO_2 led to high super saturation rate in solution, which in turn caused the formation of particles rather than nanowires. It is obvious that the hydrothermal reaction conditions and the type of precursors change the value of n and the product morphology. Because morphology and chemistry affect the final properties, synthesis of KT structures with controllable lengths and diameters has become an important issue. However, despite a variety of publications on hydrothermal growth, little is known

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about the effect of hydrothermal reaction conditions on the formation and evolution of KT nanostructures. Explanation of the mechanism behind the hydrothermal growth of these nanowires/whiskers is inadequate. The synthesis conditions have a remarkable effect on the surface properties, which in turn determines the degree of interaction of these materials within the composite matrix. Thus, detailed research is needed to understand the growth mechanism in order to control the morphology and properties of KT nanostructures.

The purpose of the present study is to clarify the factors and mechanisms underlying the growth of hydrothermally synthesized $K_2Ti_4O_9$ and $K_2Ti_6O_{13}$ nanowires. The nanowires were characterized using X-ray diffractometry (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) to elucidate the observed behavior and growth mechanism. The ultimate aim is to provide a clear understanding of the contradiction present in the literature about the mechanism of KT nanowire formation and growth at the nano scale.

Experimental Procedure

A well known TiO_2 powder (P25, Degussa) and reagent-grade KOH flakes (Sigma-Aldrich) were chosen as starting materials. 0.6 g TiO_2 powder was dissolved in 60 ml aqueous KOH solution having concentrations of 5 and 10 M using a magnetic stirrer. Complete dissolution was achieved by stirring at room temperature. Then, the aqueous solution was transferred to a reaction autoclave (UTO Engineering, Hastelloy C-276). The vessel volume was 300 ml, and the filling ratio was set to 20% by using 60 ml of aqueous KOH solution in all experiments. The autoclave system was isolated from the environment, and hydrothermal reaction was performed at 180 °C under a stirring rate of 250 rpm, at autogeneous pressures, and for reaction times 3, 12, and 24 h. After the reaction was complete, the product was taken off the autoclave, dispersed in condensed water, washed with deionized water, and filtered. Then, the products were dried in an oven at 80 °C for 12 h.

The hydrothermally synthesized products were ground gently using an agate mortar and pestle before structural and chemical characterization. XRD measurements were performed using an X-ray diffractometer (Model DMAX/B Rigaku Geigerflex) between a 2θ of 5° and 60°. A constant scan rate of 2°/min was applied at 0.02° intervals using monochromatic $CuK\alpha$ radiation with Bragg-Brentano geometry. The peak positions were indexed according to International Centre for Diffraction Data (ICDD) standards. Precise lattice parameter calculation was performed using Unit Cell® software.

Morphological analysis was conducted using a field-emission SEM (FEI Nova NANOSEM 430). TEM analysis was performed using a JEOL TEM 2100F field emission scanning/transmission electron microscope.

The products were mixed with ethanol and sonicated for 15 min. Then, a single droplet of the solution was placed on a holey carbon-coated copper grid for TEM analysis.

Results and Discussion

Phase analysis by XRD

Figures 1 and 2, respectively, show XRD patterns of the products synthesized hydrothermally under 5 M and 10 M KOH concentrations at 180 °C for 3, 12, and 24 h. The XRD pattern of P25 powder is included in the figures for comparison. The diffraction peaks of P25 powder show good agreement with the anatase (TiO_2 , ICDD: 21-1272) and rutile (TiO_2 , ICDD: 21-1276) phases. Based on the increase in hydrothermal reaction time and KOH molarity, two types of potassium titanates- $K_2Ti_6O_{13}$ (ICDD: 40-0403) and $K_2Ti_4O_9$ (ICDD: 32-0861) were formed.

The lattice parameters “a” and “c” of the anatase phase in P25 and the products synthesized hydrothermally

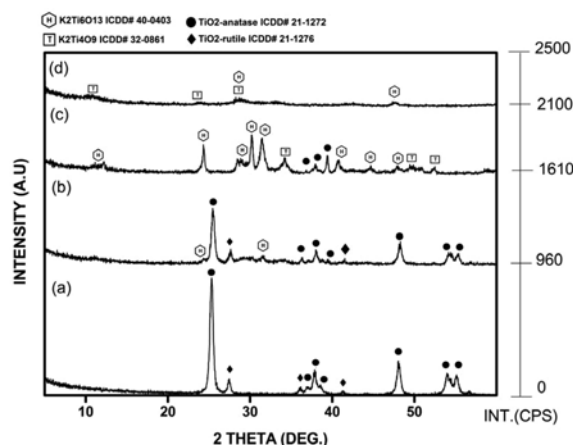


Fig. 1. XRD patterns of (a) P25, and products synthesized hydrothermally under 5 M KOH concentration at 180 °C for (b) 3 h, (c) 12 h, and (d) 24 h.

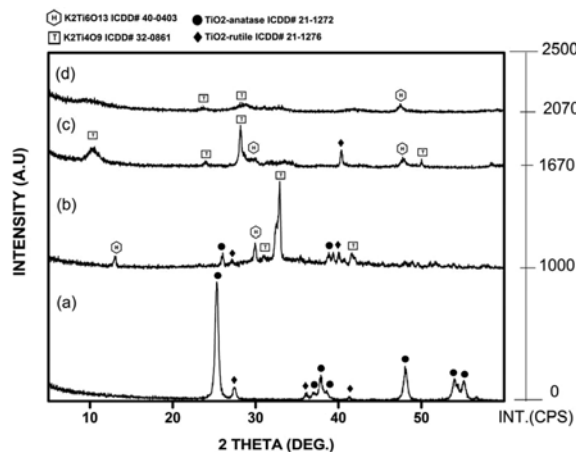


Fig. 2. XRD patterns of (a) P25, and products synthesized hydrothermally under 10 M KOH concentration at 180 °C for (b) 3 h, (c) 12 h, and (d) 24 h.

under 5 M KOH concentration were calculated from the 2θ values of the diffraction peaks corresponding to the anatase phase. All diffraction peaks of the anatase phase were considered when calculating the lattice parameters. The calculated values of anatase's parameter "a" in P25 and in the hydrothermally synthesized products under 5 M KOH concentration are 0.378 nm and 0.376 nm, respectively. The values of anatase's parameter "c" for both materials were 0.952 nm and 0.948 nm, respectively. The lattice parameters of anatase under 10 M KOH concentration could not be calculated because of the inadequate number of Bragg reflections.

The XRD pattern of the product synthesized hydrothermally under 5 M KOH concentration for 3 h is similar to that of P25. Despite the autogeneous pressure of the system, the hydrothermal reaction time of 3 h is inadequate for the formation of a sufficient amount of KTs under this KOH concentration at 180 °C. Previously, Wang *et al.* [3] stated that the optimum temperature for KT whisker formation was 300 °C, and any of the KT phases are not observed at KOH concentrations below 5 wt%. However, the present XRD data revealed that the production of KT nanostructures at 180 °C is possible by using P25 precursor and adjusting the autoclave filling ratio to 20%, which leads to an increase in pressure. The presence of small but noticeable diffraction peaks corresponding to the (110) and (311) planes in the XRD patterns of the products synthesized hydrothermally under KOH concentration of 5 M for 3 h of reaction time suggest initial formation of the $K_2Ti_6O_{13}$ phase by consumption of TiO_2 surfaces. The change in the lattice parameters of the anatase phase is an indication of the formation of $K_2Ti_6O_{13}$. The small contraction in "a" and remarkable expansion in "c" imply distortion of the anatase unit cells along the c-axis by K^+ ions for nucleating KT clusters. A similar distortion of the TiO_2 lattice and its crystallinity by K^+ was previously mentioned by Chen *et al.* [26]. The formation of an amorphous-like Ti-O-K structure might be ascribed to the increased K^+/H_3O^+ ratio, which leads to increased irregularity in the crystal structure.

As seen in the XRD pattern shown in Fig. 1(b), when the hydrothermal reaction time is increased to 12 h, $K_2Ti_6O_{13}$ crystals grow and, simultaneously, $K_2Ti_4O_9$ crystals are formed. This is verified from the increase in the peak intensities of the $K_2Ti_6O_{13}$ phase and from the appearance of peaks corresponding to the $K_2Ti_4O_9$ phase. A further increase in reaction time to 24 h caused significant peak broadening with a decrease in peak intensity indicating that the size and volume of crystallinity decreased in both phases.

Hydrothermal reactions proceeded faster when KOH concentration was increased to 10 M. The reaction time of 3 h at 180 °C was sufficient for the formation of potassium hexa- and tetra-titanate phases instantaneously, as can be seen in the XRD patterns in Fig. 2. The growth

of the (20-1) and (310) planes of hexa-titanate and the (004), (-603), and (512) planes of tetra-titanate phases is apparent. In the 12-h reaction, peak broadening was noted, especially for the tetra-titanate phase. The relatively early initiation of peak broadening under 10 M KOH concentration than that under 5 M KOH concentration means faster growth, which is significant after 24 h with a higher amount of tetra-titanate phase formation. The optimal reaction time for the formation of nanowires was taken as 24 h owing to the broadening of XRD peaks.

It is obvious that an increase in molarity increases the hydrothermal reaction rate, namely the dissolution-precipitation rate, which causes $K_2Ti_4O_9$ to form earlier. As the OH^- in hydrothermal solutions increases, the solubility of K^+ increases. Hence, the cost of nucleus formation between the crystal and the solution decreases. On the basis of the Lamer crystallization model, when the critical supersaturation limit is reached, Ostwald Ripening and diffusional growth ignite the small crystallite growth [27]. Moreover, the autogeneous pressure during the hydrothermal reaction should be considered because the autoclave filling level is a critical parameter that influences both the total OH^- in solution and the growth rate. H bonding in water is disrupted with a modest increase in the autogeneous pressure. As a result, the OH^- concentration in solution increased considerably and KT saturation became more achievable at relatively lower temperatures with reduced reaction durations. XRD data revealed that the optimum KOH concentration for nanowire formation in a hydrothermal reaction at 180 °C for 24 h is 10 M. Conclusively, the $K_2Ti_6O_{13}$ phase forms upon the deformation of TiO_2 surfaces by hydrothermal reaction and splits into smaller pieces with increasing reaction durations.

Electron microscopy analyses

Figure 3 reveals the morphological changes that occur upon the transformation of TiO_2 to KT nanowires. In the first 3 h of hydrothermal reaction, sheet-like particles were formed, as shown in Figs. 3(a) and 3(d). The transformation sequences are identical for 5 M and 10 M KOH concentrations, except for increased curvature of the formed sheets under 10 M KOH. As the reaction time increases, the sheets split and nanowires are formed. The separation surfaces of the splitting layers are shown in Fig. 3(g).

SEM analysis revealed that initial smooth surface particles converted to rough irregular shaped Ti-O-K sheets after hydrothermal treatment for 3 h under both 5 M and 10 M KOH concentrations, as shown in Figs. 3(a) and 3(d). The formation of an amorphous-like Ti-O-K structure was attributed to the increased K^+/H_3O^+ ratio resulting in increased irregularity in the crystal structure [20]. The growth of long fibrous Ti-O-K structures is observed consistently throughout the

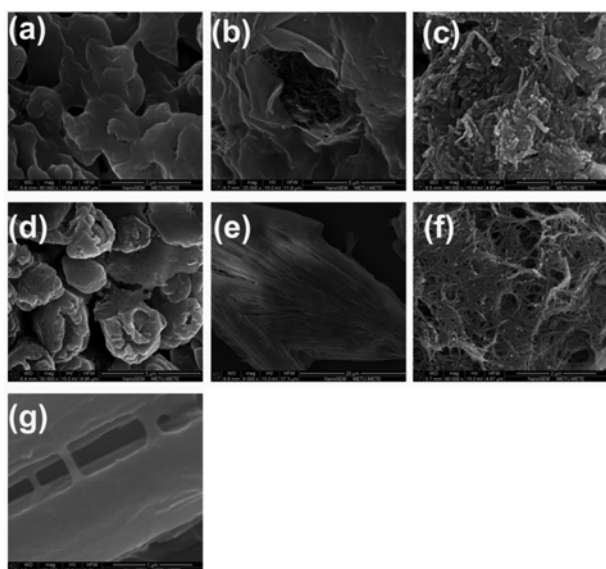


Fig. 3. SEM images of products synthesized hydrothermally under (a) 5 M KOH for 3 h, (b) 5 M KOH for 12 h, (c) 5 M KOH for 24 h, (d) 10 M KOH for 3 h, (e) 10 M KOH for 12 h, (f) 10 M KOH, and (g) splitting surfaces under 10 M KOH for 24 h at 180 °C.

product inside the amorphous sheets. The diameter of the nanowires was about 40 nm and their lengths ranged from 100 nm to 1200 nm depending on the reaction time and KOH concentration. The average diameter and length of the nanowires synthesized under 5 M KOH concentration for 24 h were 39 ± 14 nm and 286 ± 82 nm, respectively. XRD analysis revealed that the fibrous structures were composed of potassium hexa- and tetra-titanate phases. Between 3 h and 12 h of hydrothermal reaction time, the sheets stacked together and started to split into nano-structures with high aspect ratio. With further increase in reaction time to 24 h, the splitting of the sheets boosted. The nanowires synthesized under 10 M KOH concentration for 24 h had much higher aspect ratio than those synthesized under 5 M KOH concentration, although both had more or less the same diameter. The average length of the nanowires synthesized under these reaction conditions was 1140 ± 40 nm. However, identification of potassium hexa- and tetra-titanate structures from their morphologies is not quite possible.

SEM examinations confirm that the origin of nanowire formation involves a combined mechanism of oriented attachment and strain-induced splitting mechanisms by which the titanate sheets split into smaller pieces. Furthermore, the increase in the aspect ratio of the nanowires with increasing reaction time and KOH concentration without any change in the diameter clarifies that the crystal growth is one-dimensional. However, the preferential cleavage direction cannot be revealed from SEM examinations.

The TEM images of the surfaces of the hydrothermally synthesized products at 3 and 24 h are shown in Fig. 4 (b,

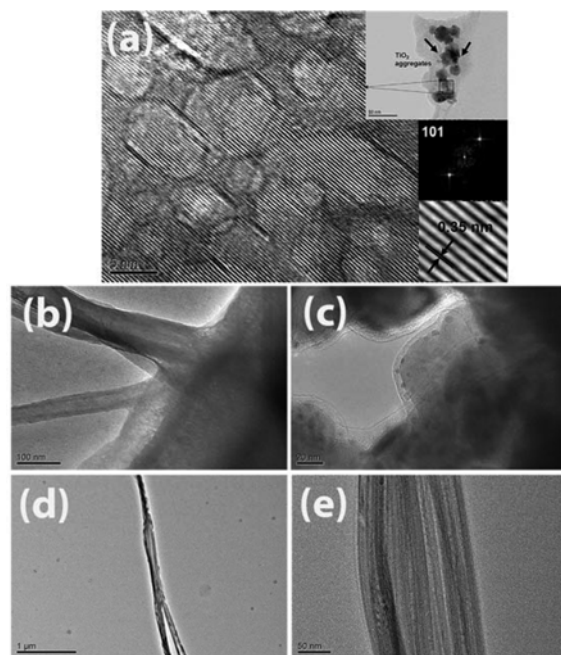


Fig. 4. TEM images of (a) P25 powder and hydrothermally synthesized products under (b and c) 10 M KOH for 3 h and (d and e) 10 M KOH for 24 h.

c) and in Fig. 4 (d,e), respectively. The TEM images of P25 powder are shown in Fig. 4(a) for comparison. The measured lattice plane spacing of 0.35 nm from the Fast-Fourier transforms (FFTs) of images (inset) corresponds to the (101) plane of the anatase phase. Initial spherical anatase particles had smooth surfaces. They were about 10-20 nm in size and were highly agglomerated.

The formation and splitting of Ti-O-K sheets are noticeable even at 3 h of hydrothermal reaction time, as shown in Figs. 4(b and c). The formation of long K-Ti-O whiskers is evident, and the splitting of smaller-diameter lamellae was observable after 24 h of reaction under 10 M of KOH, as can be seen in Fig. 4(e).

The growth of KT crystals on amorphous sheet surfaces is shown in Fig. 5(a). FFT calculations revealed that the initially formed KT crystals were $K_2Ti_6O_{13}$. The detailed high-resolution TEM (HRTEM) images of the hydrothermally synthesized products under 10 M KOH concentration for 24 h are shown in Fig. 5(b). The crystallographic orientations were determined according to the zone axes calculated using the FFTs shown. The growth direction of the nanowires in Fig. 5 is [010] along the b-axis, as stated formerly for KT whiskers [17, 25].

Figure 6 shows a detailed HRTEM image of the splitting branches of two nanowires synthesized under 10 M KOH concentration at 180 °C for 12 h. The nanowire has split from another one in a part close to region 2, most probably owing to the large strain associated with the lattice or orientation mismatch between the crystal structures. The crystal orientations of tetra-titanate nanowires in

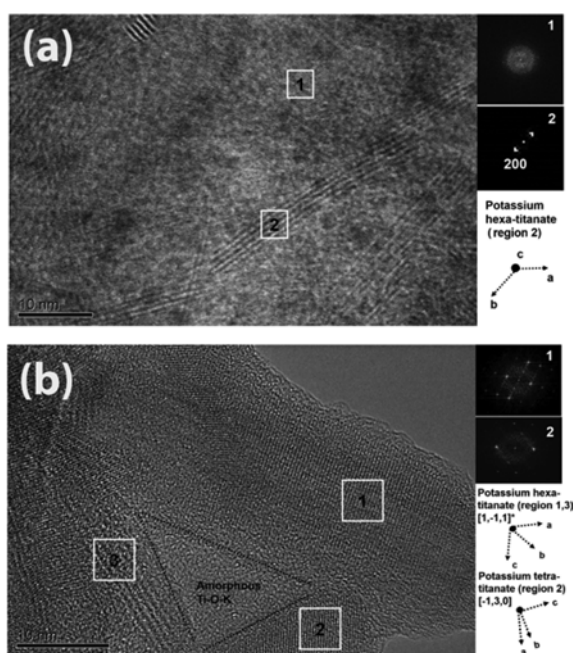


Fig. 5. TEM images and corresponding FFTs of hydrothermally synthesized products under (a) 10 M KOH for 3 h and (b) 10 M KOH for 24 h at 180 °C.

regions 1 and 2 are identical. The calculations suggest that the nanowires in region 3 could be hexa-titanate with a lattice fringe of 0.76 nm, which corresponds to the (200) plane. Nevertheless, the FFT was not adequately clear for precise calculation. The image illustrates a large strain produced on the separation region of the thinner nanowire, as shown by the arrows. The calculation was made based on the interplanar spacing difference between regions 1 and 2. Region 1 represents the strain-free part of the nanowire after splitting. FFT calculations were based on reciprocal lattice vectors representing the (201) plane of $K_2Ti_4O_9$. The amount of strain is estimated as 15% from the following equation:

$$\text{Strain (\%)} = [(d_1 - d_2) / d_1] \times 100 \quad (1)$$

where d_1 and the d_2 represent the interplanar spacing of the (201) plane of $K_2Ti_4O_9$ nanowire in regions 1 and 2, respectively.

TEM analysis revealed that some protuberances exist on the anatase surfaces after hydrothermal treatment for 3 h. Further exposition of precipitates to heat and

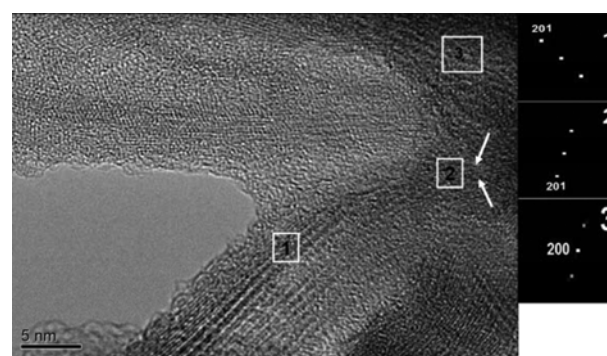
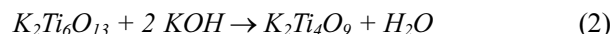


Fig. 6. TEM image and corresponding FFT of two nanowires splitting synthesized under 10 M KOH for 12 h at 180 °C.

autogeneous pressure caused the protuberances to grow and split through 10–20 nm layers, as shown in Fig. 4(e). A comparison of Figs. 4(b) and 4(d) reveals that the splitting and protuberance formation occurred simultaneously. Initial crystals formed in the amorphous-like network were $K_2Ti_6O_{13}$ crystals. This outcome supports the results driven by the XRD patterns that $K_2Ti_6O_{13}$ crystals form inside the amorphous-like Ti-O-K network that was distorted by the K^+ ions in the initial phases of the hydrothermal treatment.

A thermodynamic study of the hydrothermal reaction between $K_2Ti_6O_{13}$ and $K_2Ti_4O_9$ was performed to understand the order and type of the reaction shown:



The Gibbs free energy change ($\Delta G_{r,453}$) of the hexa- and tetra titanate phases at 180 °C was calculated using the values reported by Zhou *et al.* [28]; the results are listed in Table 1. The effect of pressure change was overlooked in the calculations because the amplitude of autogeneous pressure variation was low. Because the Gibbs free energy change ($\Delta G_{r,453}$) is greater than 0, the direct formation of $K_2Ti_4O_9$ using $K_2Ti_6O_{13}$ and KOH at 180 °C is disfavored thermodynamically under hydrothermal conditions.

The splitting of $K_2Ti_6O_{13}$ nanowires is shown in Fig. 5(b). Although $K_2Ti_6O_{13}$ nanowires split from each other, it is not clear whether the amorphous-like region forms the $K_2Ti_4O_9$ phase. Since thermodynamic calculations and the XRD results do not support a feasible hexa- to tetra-titanate transformation, tetra-titanate nanowires should be grown on the amorphous-

Table 1. Thermodynamic data for potassium titanate formation.

Material	$\Delta G_{f,298}^0$ (kJ/mol)	$\Delta H_{f,298}^0$ (kJ/mol)	C_p (J/mol · K)	$\Delta G_{r,453}^0$ (kJ/mol)
KOH ^{aq} (10M)	−378.86	−424.73	$2918.87 - 3.96 \times T + 0.0085 \times T^2$	155.33
$K_2Ti_6O_{13}$	−5849.53	−6553.32	$80.90 + 44.91 \times 10^{-3} \times T - 21 \times 10^5 \times T^2$	
$K_2Ti_4O_9$	−4054.24	−4479.98	$80.47 + 21.60 \times 10^{-3} \times T - 15 \times 10^5 \times T^2$	

like region by using the hexa-titanate phase as a nucleation site for heterogeneous crystallization. The amorphous phase on the periphery of most wires, as shown in Fig. 5(c), too, is proof of amorphous-like Ti-O-K sheets for nanowire intergrowth.

The findings conflict with those reported for the calcination method by which $K_2Ti_6O_{13}$ fibers are formed through the reaction of $K_2Ti_4O_9$ fibers with K_2O -rich liquid melt compacted in between the layers. Potassium di-titanate is the intermediate calcined product and $K_2Ti_6O_{13}$ is the high-temperature stable phase. The reaction model is called the liquid melt-inducing model because there is a remarkable amount of K_2O -rich liquid in the system upon association reactions [12]. The present results support the hypothesis that the $K_2Ti_6O_{13}$ phase is the initial phase upon formation of potassium tetra-titanates, as stated both for the hydrothermal and the sol-gel-derived reactions [19, 20]. Even so, it is not clear whether these phases form directly on the hexa-titanate phase, thus consuming its surfaces, or they form outside the amorphous-like region in this system. Du *et al.* [17] reported the formation of titanate nanowires directly on anatase surfaces matching the (101) plane of anatase to the (200) plane of $K_2Ti_6O_{13}$. However, Wang *et al.* [25] reported the formation reaction by strain-induced splitting mechanism via distortion of the TiO_2 crystal structure, leading to the synthesis of Ti-O-K sheets according to the oriented attachment mechanism in the initial phases of the reaction. As suggested by the results of FFT analysis on HRTEM images of nanowire surfaces, independent of their nature, the nanowires preferentially grew along the b-axis, extending their (200) planes. The splitting is observed to occur between both hexa-to-hexa and tetra-to-hexa nanowires. The K^+ ions were compacted between the layers/tunnels, and the lattice mismatch between them provided the driving force for splitting. The splitting originates because of the 15% strain calculated based on the difference of interplanar spacing between the splitting and the stress-free regions of the nanowire shown in Fig. 6.

Growth mechanisms of potassium titanate nanowires

The results confirm the formation of $K_2Ti_6O_{13}$ within an amorphous-like Ti-O-K structure. The transformation of KT among each other takes place via a translation mechanism between the octahedral layers. The crystal structure and orientation of the octahedral layers in KTs are shown in Fig. 7.

The formation of a relatively lower K^+ -containing titanate phase ($K_2Ti_6O_{13}$) in an amorphous-like matrix is an expected result under autogeneous pressure at short reaction durations because the sharing of three TiO_6 octahedra enclosing 2 K^+ ions/tunnel is always easier to arrange within an amorphous structure under pressure. This is the point where the calcination and hydrothermal growth theories differ from each other. A previous study by Janes and Knightley [19] and the

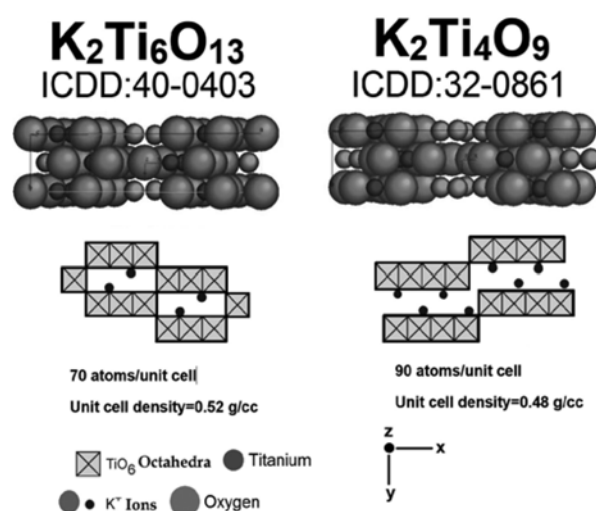


Fig. 7. Crystal structures of potassium titanates ($K_2Ti_4O_9$, $K_2Ti_6O_{13}$).

present study agree on the contention that hydrothermal and sol-gel methods involve crystallization of $K_2Ti_6O_{13}$ as an initial product inside an amorphous matrix with the help of autogeneous pressure and heat. In terms of crystalline structure, it is well known that nature prefers the lowest energy possible and forms the simplest lattice from an amorphous-like structure. For this reason, the formation of $K_2Ti_6O_{13}$ at low KOH concentrations and shorter hydrothermal reaction times is favored, as indicated by the thermodynamic calculations and TEM analysis results.

The formation of potassium n-titanates with an increase in KOH concentration after 24 h of reaction is then explained by the stoichiometric balance of Ti-K in the network and the effect of pressure linking the ribbons on their corners. For KT nanostructures formation, stoichiometric amounts of cationic K^+ and anionic Ti_xO_y ribbons, and a basic pH 8 solution are required [20]. In the present study, the basicity was regulated by the autoclave filling level, wherein OH^- was increased by increasing the solution volume and the K^+ content. Consequently, the increase in K^+ content promoted the formation of layered and high-K-containing $K_2Ti_4O_9$.

Conclusions

Different phases of KT nanostructures were synthesized via hydrothermal reaction under controlled conditions. The hydrothermal reaction temperature and time, autoclave filling level, and the type of the initial TiO_2 precursor have a profound effect on the formation and morphology of KT nanostructures. An atomic-scale analysis using HRTEM indicated the formation of KT nanowires via a combined mechanism of oriented attachment and strain-induced splitting mechanisms. The splitting of $K_2Ti_4O_9$ nanowires from $K_2Ti_6O_{13}$ was evidenced by HRTEM for the first

time. The formation reaction depends on the distribution and amount of K ions in the amorphous-like matrix. The strain associated with the variety of K ions determines the final crystal structure. Different from the calcination reaction mechanisms, tunneled structures are more likely to form from amorphous-like matrices under autogeneous pressure.

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