Hydrothermal Conversion of Self-Assembled Titanate Nanotubes into Nanowires in a Revolving Autoclave

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Titanate nanowires were synthesized through the hydrothermal synthesis route (10 M NaOH, 130 °C) from anatase in a rotating autoclave. A combined TEM, SEM, XRD, FT−Raman, and N_2 adsorption investigation of the reaction products as a function of time revealed that the 60−150 nm wide and ∼5 μm long nanowires are in fact formed by the merging of self-assembled nanotube bundles. The nanowires are able to further self-assemble into ∼5 μm wide and longer than 30 μm long, dense "superbundles" if the reaction is allowed to run long enough. We propose that the spontaneous nanotube arrangement could be caused by the rotation-assisted oriented attachment of the tubes.

Introduction

One-dimensional nanostructures have been in the focus of the materials science community for well more than a decade now.[1] Although carbon nanotubes may solve many challenges of materials engineering in the long run, at present, their practical applicability appears to be limited by the lack of adequately selective synthesis technologies. On the other hand, inorganic nanostructures (e.g., metallic nanowires, oxides, sulfides, selenides, etc.) can be prepared in a rather controlled manner, and therefore, their industrial-scale application is very close now.

High-aspect-ratio TiO_2 and titanate nanostructures are intensively studied at present because of their promising photoelectrical,[2,3] biomedical,[4] and Li^+ and H_2 storage properties.[5−8] On the basis of the pioneering work of Kasuga et al.,[9] research efforts on titanates were at first concentrated on the hydrothermal synthesis and structure elucidation of titanate nanotubes. Nowadays, nonhollow titania nanoobjects are also being investigated by several groups.[10−13] In this paper, we shall use the term "nanotube" for high-aspect-ratio objects with a hollow inner channel and diameter below 50 nm and "nanowire" for high-aspect-ratio objects without an inner void and a diameter below 200 nm. The terms "nanowhisker" and "nanofiber" are also frequently met in the literature, sometimes as synonyms of nanowire. In our terminology, nanowhiskers are characterized by a cross-section varying along the length of the object, whereas nanofibers are similar to nanowires but feature a significantly larger (above 250 nm) diameter.

Until recently, it was commonly accepted[14] that nanotubes are formed under milder reaction conditions (90−150 °C and 5−10 M NaOH) by the rolling up of exfoliated trititanate crystal sheets,[15,16] whereas higher temperature and higher alkali concentration (e.g., 200 °C and 15 M NaOH, according to Zhu et al.[17]) promote unidirectional crystal growth, leading to nanowires[18] or nanowhiskers.[19] The morphology and formation mechanism of titanate nanoentities has seen much discussion lately.[20] The most recent addition is the work of Wu et al., who proposed a uniform formation mechanism that is supposed to link all morphologies and reaction pathways into one coherent picture.[21]

We have recently succeeded in granting photocatalytic activity to trititanate nanotubes by CdS doping,[2,22] published evidence against the commonly accepted sheet roll-up

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formation model, and suggested that titanate nanotubes could form by oriented crystal growth.[23] In the course of our work, we have come across some intriguing findings related to trititanate nanotube and nanowire growth conditions. Therefore, we believe that the universal formation mechanism of Wu et al. needs to be amended by a direct low-temperature nanotube to nanowire path missing from the original publication.

In the present contribution, we show that nanotubes can be transformed directly into nanowires in a rotating autoclave at 130 °C, a temperature lower by 20 °C than the limit previously reported for nanowire formation. We suggest that the success of the synthesis is related to the spontaneous self-assembly of trititanate nanotubes with oriented attachment mechanism, which is described here for titanate nanotubes for the first time.

Experimental Section

The nanowires were prepared by mixing 2 g of anatase TiO_2 into 140 cm^3 10 M aqueous NaOH solution until a white suspension was obtained, aging the suspension in a closed, cylindrical, Teflon-lined autoclave (diameter 4 cm, height 14 cm) at 130 °C for 1−72 h while rotating the whole autoclave intensively at 60 rpm around its short axis, and finally washing the product with deionized water and neutralizing with 0.1 M HCl acid solution to reach pH 7; at this point, the slurry was filtered and the nanowires were dried in air at 70 °C.

Transmission electron microscopic (TEM) observations were performed on a Philips CM10 instrument using copper mounted holey carbon grids. The specific surface area was calculated using the BET method[24] from N_2 adsorption isotherms measured at 77 K on a Quantachrome NOVA 2000 instrument. XRD profiles were measured on a DRON 3 instrument using Cu Kα radiation. FT−Raman spectra were averaged from 256 scans performed at 4 cm^{-1} resolution on a Bio-Rad FT-Raman instrument operating with a 1064 nm excitation wavelength at room temperature in air. Scanning electron microscopy (SEM) was done on a Hitachi S-4700 field emission scanning electron microscope equipped with a Röntec energy dispersive X-ray spectrometer. The SEM samples were sputter-coated with an approximately 3 nm thick Au/Pd layer to avoid charging.

Results

We studied the effect of synthesis time on the morphology of the product of the hydrothermal trititanate nanotube synthesis in a revolving autoclave. In Figure 1a−f we present TEM images of samples synthesized in 1, 5, 8, 14, 24, and 72 h, respectively. In the beginning, we observe the transformation of anatase particles into trititanate nanotubes, just as in the case of the conventional static autoclave synthesis, only faster because of the intense mixing of the autoclave. After 5 h, the sample consists mostly of randomly oriented titanate nanotubes (Figure 1b). As the reaction advances, several individual nanotubes become aligned and construct a hierarchical bundlelike secondary structure (images c and d of Figure 1). The walls of the nanotubes forming the bundles can be clearly identified in these images. The concluding step of the reaction series is the densification of the bundles into nanowires 50−150 nm in diameter and longer than 5 μm in length. (images e and f of Figure 1). Because the length of an individual nanotube is typically less than 200 nm,[23] the appearance of 5 μm long bundles should also be regarded as proof for the high affinity of the nanotubes toward self-assembly. The end product of the reaction after 72 h is a highly crystalline nanowire with $d = 0.50 \pm 0.07$ nm interlayer spacing, as evidenced by Figure 1g. X-ray emission spectroscopy (EDX) performed within the SEM sample chamber on this sample indicated that the material was free of sodium (within the detection limit of ~0.5 at %) and featured a Ti:O atomic ratio of 1:2.26.

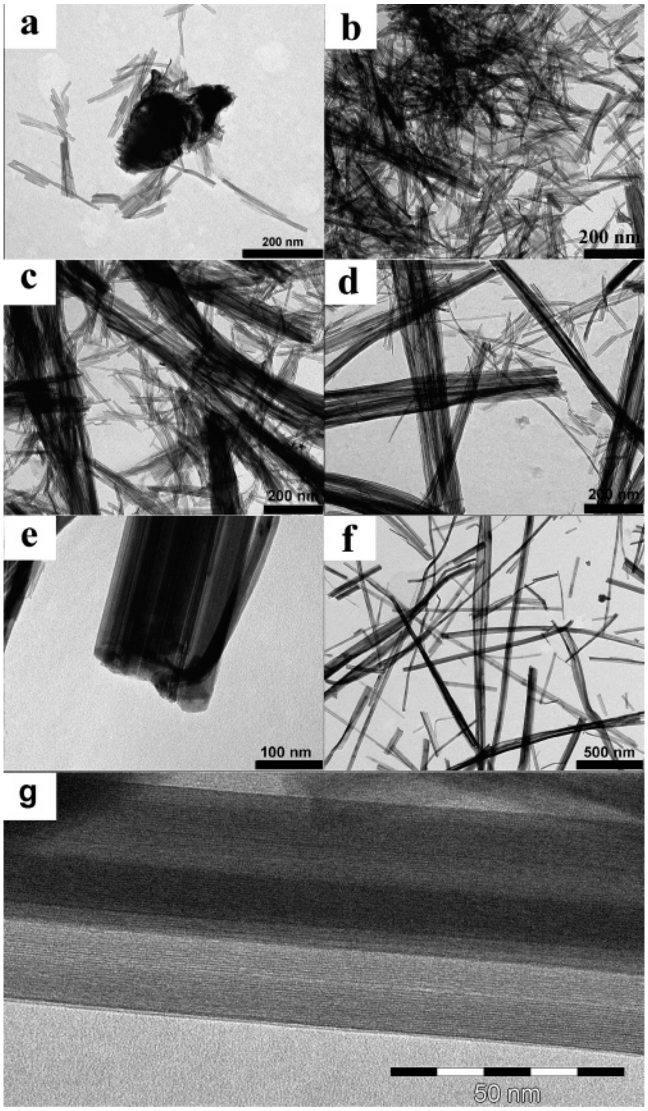

Figure 1. TEM images of the products of hydrothermal nanowire synthesis in a revolving autoclave. Images a−f correspond to reaction stages at 1, 5, 8, 14, 24, and 72 h, respectively. The layered crystalline structure of the nanowire synthesized for 72 h is observable in the higher magnification image g.

It is interesting to observe in the SEM images presented in Figure 2 that the emerged nanowires favor even further alignment into superbundles if the reaction is allowed to run longer. The transition from a loose array of individual nanowires into a compact, dense rope measuring ~5 μm in diameter and longer than 40 μm in length is apparent in

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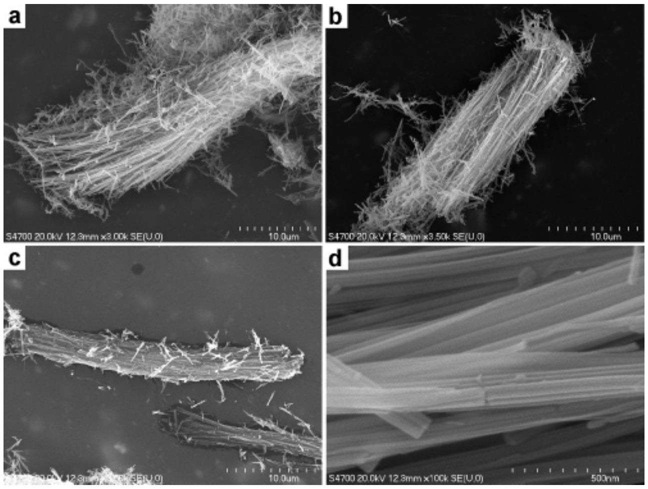

Figure 2. SEM micrographs of titanate nanowires synthesized in a revolving autoclave. Images a−c show the product after reation times of 72, 96, and 168 h, respectively. The details of the structure of the 96 h product can be observed in image d.

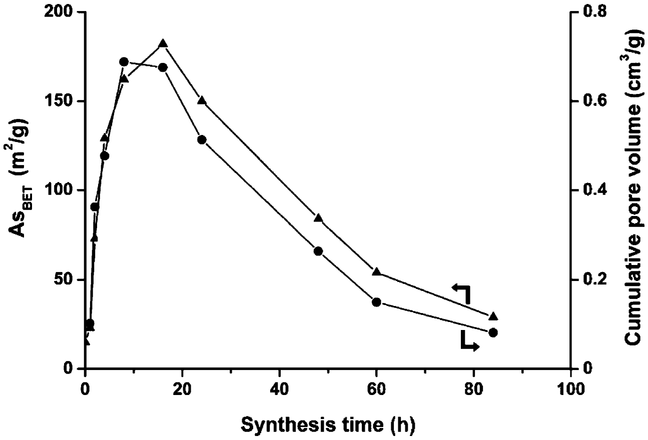

Figure 3. Time dependence of the specific surface area (triangle) and total pore volume (circle) of the products of the hydrothermal trititanate nanowire synthesis reaction performed in a revolving autoclave.

Figure 2a−c, corresponding to reaction products obtained in 72, 96, and 168 h, respectively. No further morphological changes were found when the reaction was continued for more than 168 h. The details of the structure of the 96 h product are visible in the high-resolution SEM image presented in Figure 2d. It can be seen that the primary building blocks forming the superbundle are aligned nanowires of 80−150 nm diameter. This finding matches the results of the TEM analysis (Figure 1e) concerning the diameter of the nanowires obtained by nanotube self-assembly.

The pore structure of the samples was probed by N_2 adsorption, as reported in Figure 3. In the first 18 h of the synthesis, the specific surface area increases from 8 (corresponding to the anatase starting material) to 186 m^2/g, a value typical[25] for trititanate nanotubes. Interestingly, the specific surface area of the reaction product starts decreasing after this apex and is gradually reduced to 21 m^2/g after 84 h. The cumulative pore volume exhibits a similar trend as a function of time. This behavior is different from that observed for hydrothermal trititanate nanotube synthesis in a static autoclave, as in that case, the specific surface area vs time function can usually be described as a saturation curve[26] and not a maximum one. Unusual as it is, the observed phenomenon can be interpreted in full agreement with the TEM images presented in Figure 1. We suggest that the increasing branch of the specific surface area vs time curve corresponds to the formation of hollow trititanate nanotubes from the anatase starting material, whereas in the decreasing branch, the nanotube self-assembly and densification into nonhollow nanowires take place.

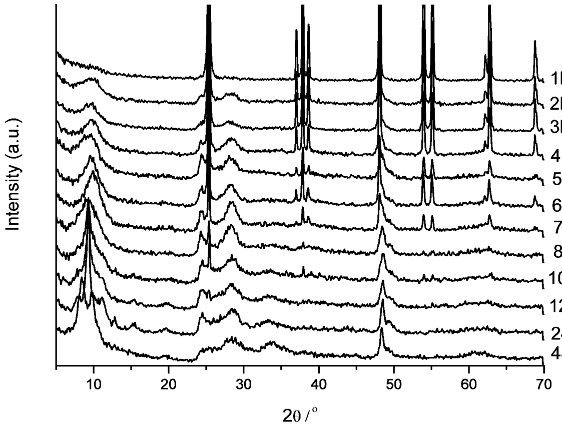

Figure 4. Evolution of the XRD profile of the products of the hydrothermal trititanate nanowire synthesis reaction with time.

The crystalline structure of the reaction products can be assessed on the basis of XRD profiles presented in Figure 4. Reflections belonging to the trititanate phase (at $2\theta = 9$, 24.5, and 28°) appear after 2 h. The total conversion of anatase into trititanate takes approximately 12 h. The nanotube to nanowire transformation is complete after 48 h, at which point the XRD pattern can be identified as $H_2Ti_3O_7$. This assignment is also supported by the EDX elemental analysis described above. No further changes to the crystal structure were found by XRD when the reaction was continued for longer than 48 h.

FT−Raman spectroscopy is a sensitive tool for monitoring structural changes in one-dimensional titania nanoobjects. In Figure 5a−e, we present characteristic Raman spectra of the unprocessed reaction product obtained from a revolving autoclave after 0, 4, 8, 24, and 84 h of synthesis time, respectively. Well-known anatase peaks at 142, 196, 397, 514, and 639 cm^{-1} dominate the spectrum at the early reaction stages (spectra a−c). However, a peak assigned to a Ti−O−M (M = H$^+$ or Na$^+$ in our case) vibration of the trititanate structure appears as early as 4 h after starting the reaction. After 8 h, the other characteristic trititanate Raman peaks assigned[27,28] to Ti−O−Ti, Ti−O−M, and four-coordinate Ti−O vibrations also become visible at 278, 660, and 905 cm^{-1}, respectively. The anatase to trititanate conversion is complete after 24 h (spectrum d), whereas the spectrum of the 84 h product (e) is typical for a well-

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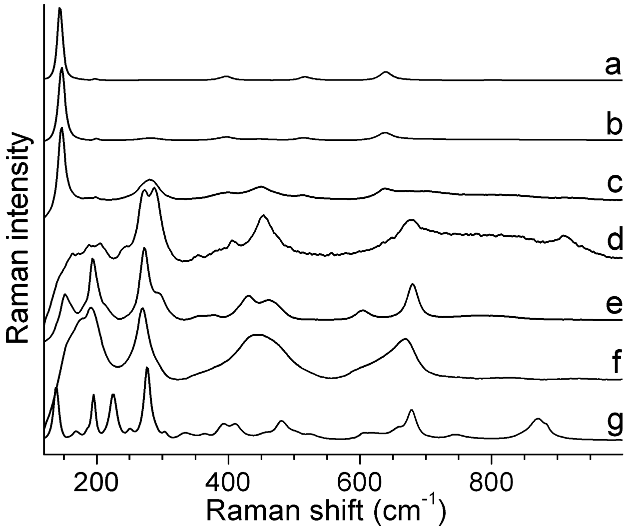

Figure 5. FT−Raman spectra of the products of the hydrothermal trititanate nanowire synthesis reaction performed in a revolving autoclave. Spectra a−e were recorded after 0, 4, 8, 24, and 84 h, respectively. Spectrum f belongs to trititanate nanowires synthesized in a static autoclave at 190 °C in 15 M NaOH. The spectrum of lamellar $Na_2Ti_3O_7$ is also presented as spectrum g for reference.

crystallized trititanate phase. This can be seen by comparing the spectrum with that of a lamellar $Na_2Ti_3O_7$ reference sample (spectrum g) synthesized following the original Andersson−Wadsley recipe.[29] It is interesting to compare the spectrum of the sample rotated for 84 h with that of a reference trititanate nanowire synthesized in the conventional way (static autoclave, 190 °C, 15 M NaOH), presented as spectrum f. Although the same peak groups can be observed for the two samples, the peaks of the material prepared in the revolving autoclave are sharper and better resolved, indicating better crystallinity. This finding is in agreement with the HRTEM image presented in Figure 1g.

Discussion

The novelty of the presented nanowire synthesis method is the rotation of the whole autoclave unit. Although agitation of the reaction vessel by stirring[30,31] and ultrasound[32] was described earlier, these researchers have not noticed any nanotube self-assembly. Some preceding occurrences of unprompted titanate nanostructure arrangement in the literature are those by Zhang et al.,[33] who described the self-assembly of octadecyltrichlorosilane covered nanotubes into nanorods held together by secondary bonding forces; Su et al.,[34] who observed nanofibers interlinking into a hierarchical intertextural structure; and Peng et al.,[35] who reported the synthesis of bundlelike nanotube assemblies at very high (above 190 °C) temperatures. The closest forerunner of the present finding is that of Nian and Teng, who reported on the hydrothermal conversion of titanate nanotubes into anatase nanorods.[36] However, their nanorods featured an aspect ratio of 6, whereas the nanowires discussed here have aspect ratios greater than 30. Moreover, Nian and Teng converted the nanotubes into anatase nanorods in a mildly acidic suspension, whereas in a parallel paper, Bavykin and co-workers described the slow transformation of titanate nanotubes into rutile nanoparticles in 0.1 M H_2SO_4.[37]

According to the universal formation mechanism of Wu et al.,[21] neither $Na_2Ti_3O_7$ nor $H_2Ti_3O_7$ nanotubes can be converted into nanowires, only into ~500 nm thick nanofibers; even that requires a hydrothermal reaction at 180 °C. In our case, nanotubes are stable without rotation for at least 168 h under their growth conditions (10 M NaOH, 130 °C). If the autoclave is rotated around the long axis, nanotubes appear fast (5 h), but their conversion into nanowires is slow: after 120 h, it is still possible to find individual nanotubes in the system. However, if the rotation is performed around the short axis, we can get high-purity nanowires within 72 h.

Let us now realize that by rotating the whole autoclave, we generate a unique flow pattern in the vessel. Unlike other agitation methods such as stirring and sonication, autoclave rotation does not introduce eddies or bubbles into the synthesis mixture. At the same time, the constant motion prevents sedimentation and forces the intimate mixing of the system. The larger the radius of the rotation, the more pronounced the mixing will be.

Two points must be addressed in order to explain the nanotube to nanowire transformation. First, why do nanotubes self-assemble into oriented bundles, and second, what happens to their hollow inner channels. Actually, the second question is easier to answer. It is widely accepted that solid nanorods are generally favored over hollow nanotubes in systems having entered the thermodynamic control regime (prolonged reaction time).[1,38] For example, the conversion of γ-AlOOH nanotubes into nanorods has been recently described by Hou et al.[39] Therefore, trititanate nanotubes can be converted into nanowires because of the free enthalphy gain achievable by reducing the surface-to-bulk ratio of the nanoobjects. This is realized through the dissolution of sodium trititanate from the most vulnerable nanotube parts (presumably the tube ends), solution-phase material transport into the nanotube channels and recrystallization within the channels to yield solid nanorods.

As for nanotube bundling, it must be related to the unique fluid course characteristic for rotating autoclaves, because it has not been described earlier for static, stirred, or sonicated systems. In a static autoclave, there is no driving force for particle reorientation, and therefore, the random aggregated structure of the primary titanate nanotubes is conserved. In this random network, particle−particle contact is not effective, and therefore, nanotubes do not bundle. On the other hand, the heterogeneous flow fields created by internal

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stirring or sonication are probably too effective in continuously breaking up freshly formed nanotube assemblies, so bundling is prevented again.

Apparently, flow conditions in the rotating autoclave are favorable for the oriented attachment mechanism to take effect. Oriented attachment has recently been found to be the relevant mechanism in the growth of several nanomaterials.[40−43] Because of the agitation, the original randomly oriented nanotube network is broken up, resulting in a parallel orientation of primary nanotubes.[44] According to Penn and Banfield, when structurally similar surfaces of particles approach, there will be a driving force to form chemical bonds between atoms of opposing surfaces so as to achive full coordination, resulting in nanotube bundles fusing along identical crystal faces and forming titanate nanobelts.[45] The total energy is decreased as a result of the elimination of the solid−liquid interface. The background of the oriented attachment theory is still under discussion. One possible explanation is based on the difference in surface structure and reactivity of the different crystal faces, whereas another elucidation is based on the induced dipole−dipole interactions at the early stage of wire formation.[45,46]

In our case, anatase recrystallazation into titanate begins with the hydrothermal coarsening of anatase nanoparticles,[47] followed by the growth of trititanate nanotubes with oriented crystal growth.[23] The nanotubes assemble into bundles by mixing-force-assisted oriented attachment. Nanotube self-assembly precedes the conversion of hollow tubes into filled objects. This is most evident from images c and d of Figure 1, where it can be seen that that the <200 nm long, hollow nanotubes arrange into >1 μm long bundles before developing a solid core. This finding emphasizes the distinction between trititanate nanotube self-assembly (governed by the mixing-force-assisted oriented attachment) and nanotube to nanowire conversion (a thermodynamically controlled process related to the minimalization of the total free enthalphy of the system). It is also in full agreement with the N_2 adsorption data presented in Figure 3, insofar as it explains the appearance of the maximal pore volume at 18 h synthesis time, when the morphology resembles bundled nanotubes still.

Conclusions

We have discovered that trititanate nanowires can be synthesized hydrothermally at lower temperature (130 °C) and NaOH concentration (10 M) than reported previously if the synthesis autoclave is rotated continuously. The obtained nanowires are identical to conventional hydrothermal trititanate nanowires with respect to morphology and crystal structure, but feature better crystallinity. The nanowire formation process was monitored as a function of time by TEM, SEM, XRD, N_2 adsorption, and FT−Raman spectroscopy. It was found that the nanowires are formed from self-assembled trititanate nanotube bundles. A possible explanation for the peculiar spontaneous self-alignment of the nanotubes can be offered by considering that in a rotating autoclave, the tubes are subject to mixing-effect-induced oriented attachment. The conversion of nanotube bundles into nanowires is a secondary process under thermodynamic control. Further research efforts will be necessary to explore the limits of the size selectivity of the self-assembly process, especially in the light of the described appearance of nanowire superbundles upon prolonged agitation.

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