

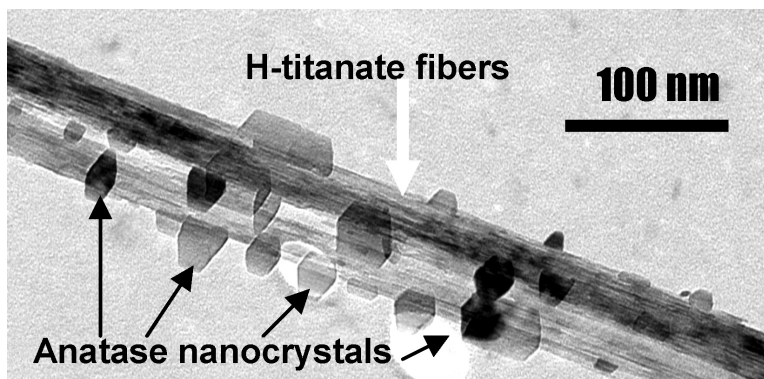
Communication

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Hydrogen Titanate Nanofibers Covered with Anatase Nanocrystals: A Delicate Structure Achieved by the Wet Chemistry Reaction of the Titanate Nanofibers

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Anatase (TiO₂) is regarded as the best photocatalyst for decomposing refractory organic pollutants in water and air.^{1–3} When they are illuminated with ultraviolet (UV) light, anatase particles produce hydroxyl radicals, by which most organic compounds can be degraded completely into carbon dioxide, water, and mineral ions.^{2,4} It is nontoxic, relatively cheap, chemically stable throughout a wide pH range, and robust under UV illumination. It can be used in various processes such as odor elimination from drinking water, degradation of oil spills in surface water systems, and degradation of harmful organic contaminants such as herbicides, pesticides, and refractive dyes. The photocatalytic reaction takes place on the catalyst surface. Therefore, catalysts of ultrafine anatase powders with a particle size at a scale of tens of nanometers should exhibit a superior activity because of the large specific surface. However, ultrafine powders have a strong tendency to agglomerate into larger particles, resulting in an adverse effect on catalyst performance. Furthermore, it is very hard to recover them after the reaction, leading to a potential difficulty in downstream separation.⁵ Continuing efforts have been made to develop alternate approaches to synthesize the structures which can be separated readily and which have the superior performance of anatase nanocrystals.⁵ In this communication we report a delicate composite structures which consist of long titanate fibers of thickness 40–100 nm and length up to 30 μm long covered with anatase nanocrystals of 10–20 nm. Importantly, this composite structure was achieved by a controlled reaction of titanate nanofibers with a dilute acid solution, and the titanate fibers were fabricated through a hydrothermal reaction of common inorganic titanium salt and a concentrated NaOH solution, rather than convention pyrolysis reaction at above 1100 K.

For instance, a solution of 10.7 g of TiOSO₄·H₂O in 80 mL of water was mixed with 200 mL of 15 M NaOH solution. The mixture was then autoclaved at 473 K for 2 days (hydrothermal reaction) to yield sodium titanate fibers. The solid in the autoclaved mixture was recovered and washed with deionized water. The obtained wet cake was then neutralized, using 100 mL of 0.1 M HCl solution, and washed with water to yield hydrogen titanate (H-titanate) fibers. The straight and curved fibers are 40–80 nm thick and up to 30 μm long, and the aspect ratio (length-to-thickness) of the fibers is over 200 (Figure 1a). The long fibers are well crystallized of layered H-titanate according to the high-resolution transmission electron microscopy (HRTEM) image of the fibers (Figure 1b). The HRTEM image is similar to those of alkali titanate.⁶ The fibril axis is in the <010> direction and the <100> direction is perpendicular to the stacking layers. The X-ray diffraction (XRD) pattern of the fibers

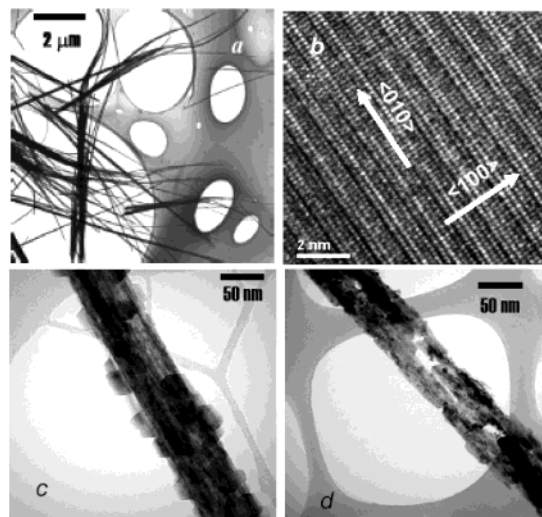


Figure 1. TEM images of the samples. (a) H-titanate fibers, (b) HRTEM image of the fibers, (c) the product of the phase conversion reaction at 373 K, a titanate fiber covered with anatase crystals, and (d) the product obtained at 393 K, fibril aggregates of anatase nanocrystals.

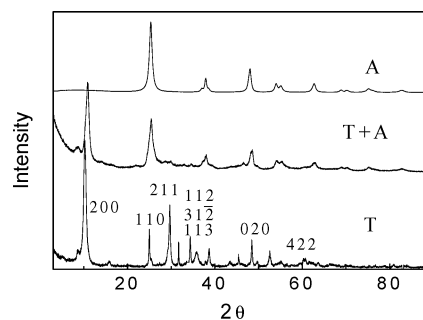


Figure 2. XRD patterns of the H-titanate nanofibers (T), titanate fibers covered with anatase nanocrystals (T+A), and the fibril aggregates of anatase nanocrystals (A).

(Figure 2, bottom) has features similar to those of alkali or hydrogen titanates with a monoclinic lattice (*C2/m*) reported in the literature.^{7,8b}

Titanates are regarded as “refractory” mineral substances and chemically stable in a wide temperature range.^{8–10} Surprisingly, the titanate nanofibers in this study can react readily with mineral acids, yielding composite structures at a scale of nanometers and aggregates of anatase nanocrystals, which retain the fibril morphology, depending on the temperature of the reaction. The H-titanate fibers were dispersed in a dilute (0.05 M) HNO₃ acid solution and kept at a designated temperature for 2 days.

Figure 1c is the TEM micrograph of the product obtained at 373 K. The parent long titanate fibers were partially converted to

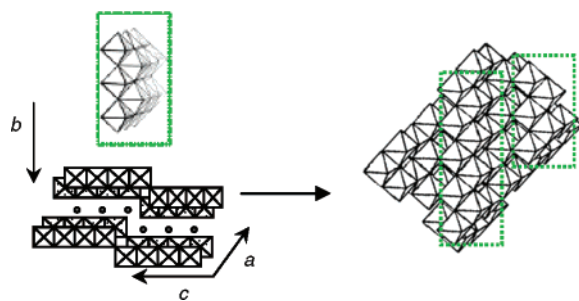
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Scheme 1. Structural Features of Titanate (left) and Anatase (right)^a



^a Both titanate and anatase contain zigzag ribbons of TiO_6 octahedra that share four edges with others (the areas in dash-lined boxes). The common features in lattice and morphology indicate that the phase transition is a topochemical reaction.

anatase. Anatase nanocrystals of 10–20 nm form over the outer surface of the titanate fiber, forming an interesting composite structure that possesses both the surface properties of anatase nanocrystals and most morphology and mechanical properties of titanate nanofibers. The partial phase transition is confirmed by the XRD patterns of the samples. The diffraction peaks from both anatase and the parent titanate can be observed in the reaction product (Figure 2). We expect that it would be complicated and difficult to deliberately create such a peculiar structure of binary composition on nanoscale.

When this reaction was conducted at 393 K in the same acid solution, the long fibers completely converted into anatase (Figure 2), yielding aggregates of anatase nanocrystals, which retain the fibril morphology (Figure 1d). These facts show that we can precisely control the reaction extent of the phase transition by regulating the reaction temperature to produce delicate new nanostructures in the wet chemistry process.

The structures of alkali titanate fibers have been studied extensively.^{6–10} The H-titanates, obtained by exchanging alkali ions with protons using dilute acid solution, can maintain the structural features of the parent alkali titanate.^{8a} In a titanate lattice, TiO_6 octahedra share edges at one level in line group, and each group is joined above and below to similar groups by further edge sharing, resulting in a zigzag ribbon structure.⁹ These ribbons join terminal corners to form layers, and sodium ions or protons exist between the layers (Scheme 1).^{8–10} We observed the layered structure from the high-resolution TEM (HRTEM) image of the fibers. The TiO_6 octahedron in such a structure share four edges with other octahedra.⁹ The zigzag ribbon and the octahedron sharing four edges are also observed in the anatase lattice (Scheme 1).¹¹ The common structural features reveal that the phase transition from titanate to anatase is likely to be a topochemical reaction process. The H-titanate nanofibers dehydrate due to the reaction with the acid, yielding anatase, and this dehydration is accompanied by an in situ rearrangement of the structural units (such as the ribbons), rather than through dissolving of titanate and atom-by-atom recrystallization of anatase. The in situ phase conversion is preferred for retaining the fibril morphology. The in situ rearrangement mechanism is strongly supported by the composite structure which is the product of incomplete conversion. This topochemical process has a low energy requirement for breaking bonding in titanate and thus can take place under moderate conditions (low temperature and low acid concentration). Such a process provides opportunities for creating delicate composite structures at nanoscale.

Both H-titanate and the composite fibers are active photocatalysts for degradation of synthetic dyes under UV light as illustrated in Figure 3. The UV source is a 100-W Hg lamp, the catalyst

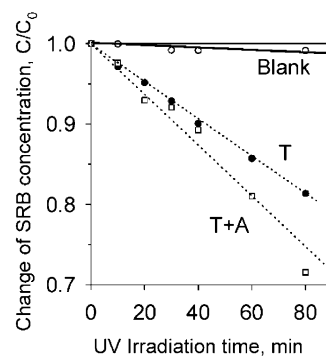


Figure 3. Photocatalytic activity of the H-titanate fibers (T) and composite fibers (T+A) for SRB degradation. The SRB concentration decreases with the irradiation time.

concentration is 0.5 g/L, and the starting concentration (C_0) of the synthetic dye sulforhodamine (SRB) is 3×10^{-5} mol/L. The composite fibers exhibit a better activity. They can be readily separated from fluid by filtration or sedimentation because their lengths are at scale of several tens of micrometers. The composite structure is ideal for the application of anatase photocatalysts at industrial scale, which has been seriously impeded by the high cost for separating the catalyst nanocrystals.⁵ We can further optimize the photocatalytic, separating, and mechanical properties of the composite fibers by controlling the extent of the phase conversion to meet the need of applications.

In summary, the hydrogen titanate nanofibers can be synthesized by a hydrothermal reaction. These fibers are chemically reactive, readily reacting with dilute acid. The product and reactant have common features in lattice and morphology, so that this reaction is a topochemical reaction, and the product retains the fibril morphology of the titanate nanofibers. We can precisely control the reaction extent, to achieve delicate composite structures at nanoscale with desired photocatalytic and separation properties. These findings highlight opportunities to create delicate inorganic nanostructures with advanced functions by wet chemical approaches.

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Supporting Information Available: UV/visible spectra of the samples. This material is available via the Internet at <http://pubs.acs.org>.

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