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Hierarchical interlinked structure of titanium oxide nanofibers

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A novel hierarchical interlinking structure of titanium oxide nanofibers with high surface area has been prepared by a soft hydrothermal chemical process *via* the reactions of amorphous TiO_2 gel (or commercial $TiOSO_4$ particles) and NaOH solution.

Low-dimensional nanostructured materials have attracted much attention due to their unique physical properties and their potential applications, including optoelectronic nanodevices. The tubes, wires or fibers within a nanometer scale are expected to possess novel properties.[1] However, the forms of most of the reported nanostructured materials are individual and/or free-standing, and little attention has been paid to the interconnected forms. If these individual nanomaterials can interconnect to integrate the nanodevices, it should be quite significant and practically useful on the nanoelectronics and optoelectronics and for information storage.[2] Searching for interconnects is a challenge to future nanoelectronics.[3] In this communication, we report the preparation of titania nanofibers by a soft hydrothermal chemical process. The nanofibers are well-interlinking. Specially, this interlinked structure of nanofibers has a large special surface area and is thermally stable, and can be used as a substitute for hazardous asbestos material,[4] as well as other applications.

Titania is a *n*-type semiconductor and a typical photocatalyst, attracting much attention from both fundamental and practical viewpoints.[5] To explore novel approaches for the nanostructured titanium oxides of various nature by controlling their nanoscale size and morphology is of great interest. TiO_2 tubes[6–8] and fibers[9,10] have been prepared using a sol–gel template processing and their diameters were normally large (> 70 nm). Smaller TiO_2 tubes with a diameter of ~ 8 nm were also reported,[11] although their structure and formation mechanism are still not fully understood.[12] The titania nanomaterial reported herein has a different form from all known forms.

The hydrolysis of an ethanol solution of titanium triisopropoxide [$Ti(OPr^i)_4$] gave, after aging, the precipitation of amorphous TiO_2 gel. The hydrolyzed amorphous gel, after drying, was used as the TiO_2 precursor for the wet chemical nanoparticle preparation. 0.1–0.3 g of the precursor was mixed with 20 ml of NaOH aqueous solution with a concentration of 5, 10 or 15 mol L^{-1}, followed by hydrothermal treatment at 100–180 °C in a Teflon-lined autoclave for 48 h. The treated powders were washed thoroughly with distilled water and 0.1 mol L^{-1} HCl aqueous solution until the pH of the washing solution was < 7, and subsequently filtered and dried at 100 °C *in vacuo* for at least 10 h. The products were characterised by using powder X-ray diffraction (XRD), N_2 adsorption analysis, energy dispersive X-ray spectroscopy (EDS) and high resolution transmission electron microscopy (HRTEM).

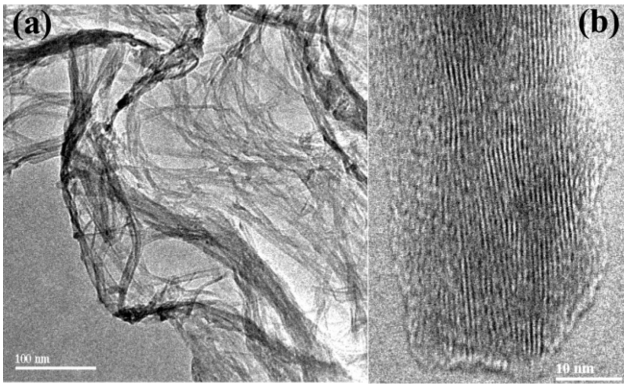

Fig. 1 (a) Low-magnification TEM image of titanium oxide nanomaterials, showing well-interlinked structure; (b) HRTEM image of a nanofiber, revealing the layered structure.

Fig. 1(a) shows a low-magnification TEM image of the obtained titania nanofibers. A large number of nanofibers with thickness of 5–30 nm and length of a few tens to several hundreds of micrometres are interlaced to form an *intertexture*-like hierarchical structure. Most of nanofibers have a curl-shaped morphology, and the surface of the nanofibers is uneven. Fig. 1(b) shows a HRTEM image of a nanofiber, indicating that nanofibers are composed of layered structure. A fringe spacing of about 0.7 nm can be seen in the lattice resolved image, which is similar to the shell spacing of TiO_x nanotubes reported very recently.[12] In addition, many defects and dislocations were also observed in the stucture of the nanofibers (Fig. 1(b)).

XRD patterns shown in Fig. 2 support the HRTEM results of the layered structure. The patterns are similar to that from the TiO_x nanotubes,[12] though no hollow nanotubes were found in our specimens synthesized from amorphous TiO_2 instead of crystalline titania. EDS of the samples revealed that they consist of titanium and oxygen. Our preliminary results suggest that the structure of the present nanofiber materials is similar to that expected for a layered titanate of nominal formulation $H_2Ti_nO_{2n+1}$, probably an analogue of titanate $H_2Ti_3O_7$.

Nanoscale fibrous structures can be obtained with good yields when the hydrothermal temperature is in the range 80–180 °C. When the temperature is higher than 180 °C, the products are mainly thin ribbon-like with width 30–200 nm and with lengths of several micrometres to several tens of

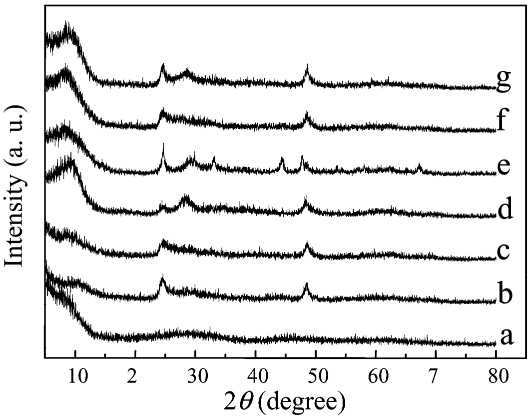

Fig. 2 XRD patterns: (a) amorphous TiO_2 precursor; (b)–(d) products from amorphous TiO_2 gel treated with 10 mol L^{-1} NaOH solution at 150, 130 and 100 °C, respectively; (e) calcined sample of (d) at 540 °C; (f) (g) products from $TiOSO_4$ treated with 10 mol L^{-1} NaOH at 100 and 150 °C, respectively.

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micrometres.[13] Changing the concentration of NaOH to 5–15 mol L^{-1} did not affect the structure of the products. Diluted NaOH solution did not result in the formation of titania nanofibers. It is interesting that commercial $TiOSO_4$ powders can also be used as the starting materials to produce nanofibers with similar interlinked structure and composition. When NaOH was replaced by KOH in the solution some titania nanofibers could also be obtained. However, those nanofibers did not interlink with each other to form an *intertexture*-like hierarchical structure.

N_2 adsorption–desorption isotherms of the synthesized nanofibers revealed the presence of mesopores (Fig. 3), probably arising from the interparticle space, meshy holes of intertextural nanofibers. BET surface areas of these fibrous materials are quite high, values of 267, 354 and 375 m^2 g^{-1} being obtained when amorphous TiO_2 powders reacted with NaOH (10 mol L^{-1}) solution at 100, 130 and 150 °C, respectively. Values of 325 and 371 m^2 g^{-1} obtained when $TiOSO_4$ powder was used as raw material and treated with alkali solution at 100 and 150 °C, respectively. It is expected that such interlinked titania nanofiberous materials will attract interest in catalysis. Investigation of their optical properties and possible applications in photocatalysis and as catalyst supports are currently being carried out. It should be significant if the fibrous materials are thermostable or thermo-resistible. HRTEM observation revealed that the microstructural layered stripes still exist after calcination at 540 °C, and the morphology of nanofibers remain unchanged, though surface decomposition may accour during high-temperature calcination.

It has been reported that titania nanotubes could be obtained when the crystalline titania (eithor anatase or rutile or their mixed phases) was reacted with a concentrated NaOH solution.[11,12] The crystalline structure of these TiO_2 polymorphs can be described in terms of representative TiO_6 octahedra which share vertices and edges to build up a three-dimensional framework. Kasuga *et al.*[11] believe that the crystalline raw material is first converted to an amorphous product through alkali treatment, and subsequently, titania nanotubes are formed after treatment with distilled water and HCl aqueous solution. However, in the present work, amorphous TiO_2 gel was directly used to react with NaOH solution under hydrothermal conditions, resulting in well-interlinked nanofibers instead of nanotubes. Titanium in the amorphous gel is octahedrally co-ordinated by two types of oxygen atoms, one type is linked with titanium atoms of adjacent octahedra, while the second occurs as O–H groups, possessing a different structure from crystalline titania polymorphs. When reacted with NaOH, some of the Ti–O–H (and Ti–O–Ti) bonds are broken by the action of the NaOH solution to generate new coordinations. The octahedra then interact with each other to give long-range order, partly transforming into layered structures of titanate composed of octahedral TiO_6 units. Simultaneously thin nanosheets of titanate are exfoliated, and with the process of hydrothermal reaction, more and more nanosheets can be formed with oriented growth. Some of individual sheets may merge to form nanofibers and further interlink into a hierarchical intertextural structure. After washing with water and dilute acid solution, Na^+ ions are exchanged and the acidic form $H_2Ti_nO_{2n+1}$ was obtained. The intertextural structure of the nanofibers formed during the hydrothermal process, as revealed by the observation of the sample without HCl-washing. Calcination at high-temperature causes dehydration and partial damage of the structure, resulting in amorphization of nanofiber surface layers. Similar phenomena took place when $TiOSO_4$ was used as the raw material, since two of oxygens in the octahedral TiO_6 units were coordinated with SO_4^{2-} in place of another titanium atom of adjacent octahedra in crystalline titania. We believe that local order of the structure of the raw materials may be important to form oriented nanostructures of shaped oxides.

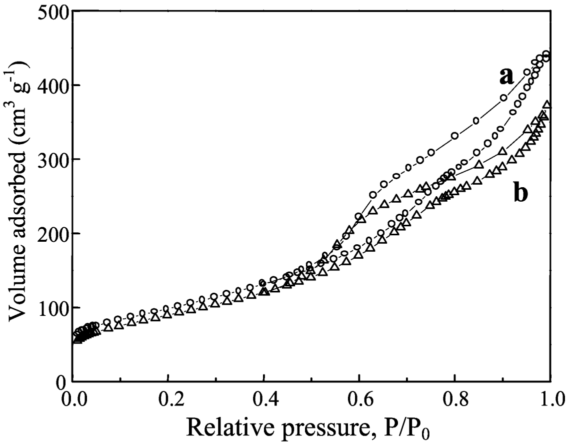

Fig. 3 N_2 adsorption–desorption isotherms of nanofibers obtained (a) from amorphous TiO_2 gel at 130 °C and (b) from $TiOSO_4$ at 100 °C.

Moreover, most of nanofibers interlink chemically rather than physically (*cf.* musculoskeletal nerve fibers). The existence of defects may result in a flexibility in structure of the titania nanofibres. Thus, the present fibrous materials may be used as functional biocompounds in bone bonding implants for bone-tissue engineering.

The preparation of titania nanofibers can also be performed by the aid of microwaves or a sonochemical process.[14] Similar interlinked forms have been observed in our preliminary experiments of microwave activated hydrothermal fabrication.[13] It is expected that the physical properties of the present titania nanofibers could be modified and improved for potential applications *via* optimization of the experimental methods. Lithium intercalation[15,16] may lead to functionalisation of the titania nanofibers for future applications as electrode materials in rechargeable lithium-batteries, fuel cells, as a separator of oxygen and nitrogen in the air, *etc*.

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