

A simple approach to mesoporous fibrous titania from potassium dititanate†

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A new approach is developed to synthesize mesoporous fibrous titania from the sintered product of $K_2Ti_2O_5$, which involves a novel hydrolytic reaction for the formation of potassium-rich nanophase and the generation of an amorphous intermediate.

The synthesis of nanostructured materials with specified and well-defined pore structures offers a new possibility for the creation of catalysts that are effective in many technological processes.¹ In particular, porous TiO_2 is of considerable interest for potential applications in highly efficient catalysts, photovoltaic cells, electrochemical photolysis of water, and semiconductors.² Since mesoporous TiO_2 was firstly prepared by a sol-gel synthesis in 1995, different self-assembly synthetic strategies have been developed using a variety of surfactants or organic molecules as templates.³ However, these procedures are very elaborate, the initial raw materials are expensive and even cause environmental pollution, which strongly limits the practical production on a large scale.

It is known that various forms of TiO_2 can be prepared from two-dimensional layered titanate and intercalation techniques. Through ion-exchange reaction of layered potassium titanate and subsequent calcination procedure, monoclinic titania, anatase or rutile with fibrous morphologies can be prepared.⁴⁻⁶ But the specific surface area of such TiO_2 is lower than $30\text{ m}^2\text{ g}^{-1}$ and no mesoporous structure exists. Recently, it has been reported that the hydrothermal reaction of the layered protonic titanate in methanol, *n*-butanol or glycerine *etc.*⁷ and the pillaring of some species into the interlayer space can give rise to an increase in the specific surface area of TiO_2 .⁸ Moreover, the exfoliated nanosheets of layered protonic titanate are used as building blocks to construct titanate nanohybrids and porous structured materials.⁹ However, the resulting products from such methods mainly consist of micropores. Herein, we report a new approach to the synthesis of mesostructured fibrous TiO_2 from layered $K_2Ti_2O_5$, which involves a novel hydrolytic step for the mesoscopic microphase separation. The resultant potassium-rich nanophase exists in an amorphous intermediate and can be easily removed by acid washing. The final mesoporous structure is composed of interconnected nanosized titania grains and can be preserved after calcination at 773 K.

The present procedure to prepare the mesoporous fibrous titania is as follows: A reactant mixture with a TiO_2/K_2O molar value of 1.9 was prepared by uniformly adding K_2CO_3 (reagent grade) to $TiO_2 \cdot nH_2O$ and then sintered at 810 °C for 2 h. The sintered product was wet ground and dried at 60 °C, then 10 g of the product was soaked in 7 ml of distilled water at ambient temperature in a closed container for about 7 days, during which the potassium-rich nanophase gradually formed. When the product was totally transformed to the amorphous phase, which was detected by the XRD pattern, the resultant product was suspended in 100 ml of vigorously stirred 0.1 M HCl solution until K^+ ion was totally removed. Then the product was separated by filtration and washed with distilled water, followed by drying in a desiccator and

at 60 °C under vacuum. Calcination of the dried titania sample was conducted in a muffle oven at elevated temperature in air for 2 h.

The phase constitutions of as-prepared sample in different synthesis steps were characterized by XRD patterns (Bruker D8, Cu-K α radiation). From Fig. S1 in the ESI,† the characteristic peaks of the sintered product disappear in the hydrolytic reaction, assigned to the phase transformation from $K_2Ti_2O_5$ to noncrystalline product A diffuse diffraction peak at $\sim 5^\circ$ in the hydrated product indicates the appearance of the potassium-rich nanocrystallite. The amorphous structure is maintained after K^+ ions have been removed by acid washing, but the reflection at lower angle disappears, suggesting the degradation of the microstructure. Upon calcination, a sharpening of the diffraction peaks of the anatase sample was clearly observed, reflecting the crystallite growth of titania fibers from the amorphous structure (Fig. S2 in the ESI). The mean crystalline sizes of the anatase nanoparticles at different temperatures, calculated by the Scherrer equation, are reported in Table 1.

The porosity of the titania materials was investigated using nitrogen adsorption-desorption isotherms (Micromeritics ASAP 2000). Fig. S3 gives the nitrogen adsorption-desorption isotherm of the calcined samples; all samples show type IV-like isotherms, indicating the presence of well-developed mesoporosity in the samples. The insert to Fig. S3 shows the pore-size distribution plots calculated by the BJH (Barrett-Joyner-Halenda) equation from the adsorption branch of the isotherm. The pore size distribution (PSD) measurements show that the average pore diameter of calcined samples has the mesoporosity of a very narrow pore-size distribution. The typical values for the specific surface area, the average pore diameter and the pore volume of all samples are summarized in Table 1. The increase of the pore diameter and the decrease of the specific surface area of the calcined samples with elevated temperature are probably due to the growth of TiO_2 crystallites. However, the values of total pore volume do not decrease, indicating that a further temperature increment could not result in the collapse of the pore system.

SEM analyses (JEOL JSM-5900) were performed to examine the morphology of the 773 K calcined sample. The rod-like particles with uneven surfaces and sizes of 5–20 μm are present in Fig. 1A, and consist of aggregated bundles of inter-grown, very narrow parallel fibers with $\sim 0.2\ \mu\text{m}$ in width in the higher magnification image (Fig. 1B). The fibrous morphology is similar to that of $K_2Ti_2O_5$ used as the precursor material.

High resolution TEM (Fig. 1C) (JEOL JEM-2010) images of the 773 K calcined sample that was recorded perpendicularly to the growth axis of the fibers show that the fibrous titania are comprised of interconnected titania nanocrystallites. The dark

Table 1 Textural properties of titania samples after calcination at different temperature

Calc. T/K	Crystalline size/nm	$S_{\text{BET}}/\text{m}^2\text{ g}^{-1}$	$V_{\text{p}}/\text{cm}^3\text{ g}^{-1}$	D_{BJH}/nm
573	7.1	206	0.23	4.5
673	7.9	187	0.24	5.5
773	9.5	139	0.27	8.7

† Electronic Supplementary Information (ESI) available: XRD patterns, nitrogen adsorption-desorption isotherms, SEM image and the photocatalytic activity of the sample. See <http://www.rsc.org/suppdata/cc/b4/b408609k/>

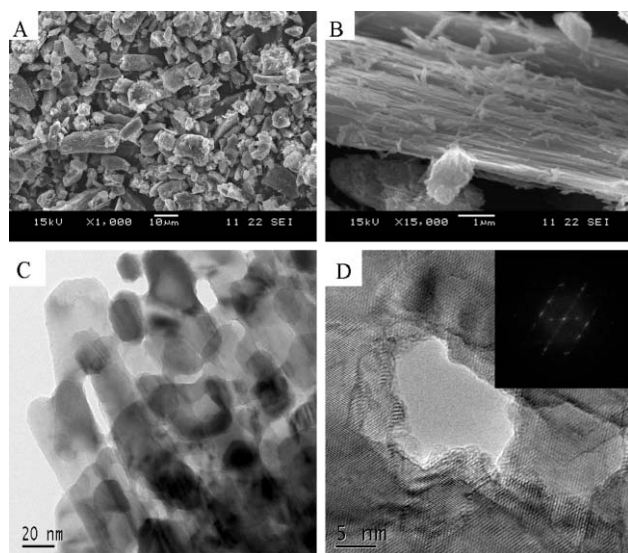


Fig. 1 SEM and HREM images in different magnification scale of the mesoporous fibrous titania after calcination at 773 K.

spots approximately in 10–20 nm diameter in the image correspond to TiO_2 nanocrystallites, and the crystalline size is in agreement with that calculated by the Scherrer equation. Stereo images show that voids ~ 10 nm in diameter are packed aligned throughout the bulk of the fibers to form a three-dimensional mesoporous structure. But no discernible long-range order in the pore arrangement exists among the fibers. The HRTEM image recorded on an individual void (Fig. 1D) and its selected area electron diffraction (SAED) pattern (inset in Fig. 1D) obtained on this image area are viewed along the [001] zone axis, showing that all anatase nanoparticles have the same crystallographic orientation since the electron diffraction spots are obviously observed.

Wallenberg *et al.* have reported that the high specific surface area of TiO_2 in the range of $10\text{--}30\text{ m}^2\text{ g}^{-1}$ with voids of 4 nm can be prepared by hydrolysis of titanate followed by thermolysis. They assumed that the voids are formed by removing potassium and water from $\text{K}_2\text{Ti}_4\text{O}_9$.⁵ Unfortunately, the essential role of $\text{K}_2\text{Ti}_2\text{O}_5$ is neglected. It is known that $\text{K}_2\text{Ti}_2\text{O}_5$ has a unique layered structure composed of trigonal bipyramids with TiO_5 units where five oxygen anions coordinate to one titanium,¹⁰ which is easily hydrated *via* the intercalation of water¹¹ and even decomposes rapidly in moist air.⁶ In most reports, the sintered product is directly added to the acid solution for ion-exchange reaction between K^+ ions in the layer and H^+ ions in the solution. Therefore, it can not cause the formation of a mesostructure because of the absence of any nanophase. In this study, massive loss of K^+ ions in ion-exchange reaction is effectively avoided by using little water during the hydrolytic reaction of $\text{K}_2\text{Ti}_2\text{O}_5$. Alternatively the hydrolytic reaction can also be achieved in moist air over a much longer time. As the layered structure of $\text{K}_2\text{Ti}_2\text{O}_5$ is destroyed by water, K^+ ions are spontaneously enriched and the potassium-rich nanophase appears. Moreover, such two procedures simultaneously occur and mutually promote. When $\text{K}_2\text{Ti}_2\text{O}_5$ is totally transformed to an amorphous phase, the amorphous titania and the potassium-rich phase, which might be KOH deducing from the reaction course, are two interdispersed phases on the nanometre scale, forming a nanocomposite structure. The mesoporous TiO_2 is created by the subsequent dissolution of the potassium-rich nanophase with the acid solution.

In addition, $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ used as a reactant, in comparison with

anatase or rutile, is more reactive so the reaction starting temperature can be lowered and the crystal-growth conditions changed.¹² Moreover, potassium titanate fibers normally have a lamellar structure on the nanometre scale along the longitudinal direction.¹³ With a short sintering time and excess potassium content in reactants during the solid state reaction, the sintered product is loose in texture, therefore $\text{K}_2\text{Ti}_2\text{O}_5$ is more easily decomposed in the hydrolytic process. All these factors may favor the formation of the potassium-rich nanophase and the final mesostructure. However, the sintering temperature has no significant effect. When the sintering temperature increases up to $970\text{ }^\circ\text{C}$, the mesoporous structure can also be obtained by the same procedure and the sample exhibits well-defined separated fibrous morphology (Fig. S4 in the ESI). Although the mechanism of formation of the mesostructure is not fully clear and is still under investigation, this work presents an easy method to fabricate mesoporous titania.

The photocatalytic activity of the calcined samples was investigated with methyl orange in a Pyrex reactor at $25\text{ }^\circ\text{C}$ by a 300 W Hg lamp. The 773 K calcined sample shows about 10% higher photodegradation activity than the commercial titania (Degussa P-25) (Fig. S5 in the ESI). Furthermore, the morphology of the mesoporous particles in the micrometre-size range is favorable for separation.

It is also interesting to note that this method reveals the mesoscopic microphase separation of inorganic species, which makes possible the synthesis of other mesostructured inorganic compounds.

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