Chem. Mater. **2003,** *15,* 4633−4636

Preparation of Composite Anatase TiO_2 Nanostructure by Precipitation from Hydrolyzed $TiCl_4$ Solution Using Anodic Alumina Membrane

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Received June 18, 2003. Revised Manuscript Received August 28, 2003

Composite anatase TiO_2 nanostructure, consisting of both tubules and rods, has been synthesized by precipitation from hydrolyzed $TiCl_4$ solution using an anodic alumina membrane (AAM). SEM analyses show that the structure consists of rods of 200−250-nm diameter and tubules of about 500-nm diameter. Each tubule may be visualized as a single sheet of 60−80 nm thickness rolled into a cylinder of diameter about 2.5 times the pore size of the AAM. The thus-prepared TiO_2 nanomaterial is characterized and a possible mechanism of its formation is discussed.

Introduction

Hydrolysis of $TiCl_4$ is the process commonly used for obtaining highly porous rutile TiO_2 films for dye-sensitized solar cells,[1] although other methods (e.g., chemical vapor deposition and sputtering) are available for preparing the films.[2] The method can yield either anatase[3,4] or rutile[1,5] TiO_2, depending on the synthetic conditions. Rutile is formed when $TiCl_4$ is added to pure water, resulting in a low pH solution,[1,5,6] whereas anatase can be formed in the presence of other components in the reaction mixture (e.g., poly(alkylene oxide) block copolymer[3] or sulfate ions[4]).

It is important to develop synthetic methods in which the morphology and the structure of nanotitania can be controlled or the fine structure can be mimicked at the nanoscale, owing to its technological importance, which in turn is due to its strong oxidizing power, chemical inertness, and nontoxicity. Templating method is one of the approaches to attain these confinement structures on a sub micrometer scale. It is also an effective way to obtain macroporous structures and thereby larger surface area. TiO_2 nanomaterials find several applications, e.g., in solar cells, photocatalysis, and other functional devices. Martin[7] is exploring template-synthesized fibrils and tubules for applications to biosensors, bioencapsulation, energy production, and electronic and electrooptical devices.

In the past decade, there has been considerable interest in the strategy of using alumina membrane, pursuing different methods of preparation of TiO_2 nanomaterials.[8−13] Lakshmi et al. have described the first use of sol−gel chemistry to prepare semiconductor nanofibrils and tubules within the pores of an alumina template membrane.[14] TiO_2 nanowire arrays have been synthesized from anodic oxidation of hydrolyzed $TiCl_3$ within a hexagonal close-packed nanochannel alumina on an Au substrate[12] or from tetrabutyltitanate in anodic aluminum oxide template by a sol−gel method.[13] The nanowires are assumed to nucleate at the center of alumina pores and expand toward the pore walls gradually, due to the electrostatic repulsion between the positively charged alumina template and hydrolyzed $TiOH^{2+}$. Depending on the composition of the sol, TiO_2 nanowires or nanotubes are synthesized with titanium isopropoxide using AAM as template.[9,11] TiO_2 nanotubes have also been synthesized by hydrolyzing TiF_4, but their formation is not assisted by an AAM template, inasmuch as the average outer tube diameter is smaller than the average channel diameter, although AAM can provide initial nucleation sites for the unconstrained growth.[8] TiO_2 nanomaterials prepared within AAM crystallize as anatase. However, a polymer gel templating procedure[15] with titanium isopropoxide or a hydrothermal method[5,16] using an aqueous solution of $TiCl_4$ yields a mixture of anatase and rutile TiO_2.

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10.1021/cm030541y CCC: $25.00

In this paper we report the preparation of a unique nanostructure of anatase TiO_2, consisting of both tubules and rods, from hydrolyzed $TiCl_4$ solution using an anodic alumina membrane, and propose a mechanism for its formation by monitoring the shape and size of it with the help of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The membrane used contains cylindrical pores with mesoscopic diameters. Obtainment of tubules and rods of anatase TiO_2 in a single process in this case, as against rutile TiO_2 without the membrane, is interesting. The unusually larger diameter of the rod−tube-composite compared to that of the pore of the AAM, and the separation of the whole nanostructure from the template, are important aspects of the paper.

Experimental Section

The fabrication of TiO_2 nanomaterial was followed from the literature,[1] except that an anodic alumina membrane (AAM) (Anodisc 13, Whatman, 200 nm) was used as a template. The nanomaterial was grown on the inside surface of the AAM by precipitation from hydrolyzed $TiCl_4$. Hydrolyzed clear solution of 0.2 M $TiCl_4$ was loaded on top of a piece of AAM placed on a filter paper within a porcelain crucible, and aspirated for about 2 h at room temperature by using an aspirator. It is to be emphasized here that the aspirator was used only for filling the hydrolyzed $TiCl_4$ into the pores, as it was not otherwise possible by gravity alone. The soaked membrane was placed vertically in a porcelain boat and heated in an oven for 2 h at 50 °C to accelerate the precipitation, which otherwise takes about 3 d at room temperature. The membrane was then treated with 3 M NaOH to remove it completely. The resulting material was washed with distilled water and annealed at different temperatures for 2 h. The product was characterized by using a Hitachi S-4300 FE-SEM, a JEOL JEM-3000F high-resolution transmission electron microscope, and a Jasco NR 1100 Raman spectrophotometer.

Results and Discussion

When TiO_2 films are grown on ITO or F:SnO_2 by precipitation from hydrolyzed $TiCl_4$ at room temperature followed by annealing between 100 and 450 °C, they consist of randomly connected, ellipsoidal clusters that are, on average, about 1.2 μm long and 0.7 μm in diameter. Furthermore, the TiO_2 particles crystallize as rutile regardless of their annealing temperature.[6,17] In contrast, the TiO_2 nanomaterials prepared within AAM in this study show different morphology and crystalline phase, obviously caused by the templating action of the membrane. EDX data and Raman spectra confirm that the nanomaterials consist of titanium dioxide.

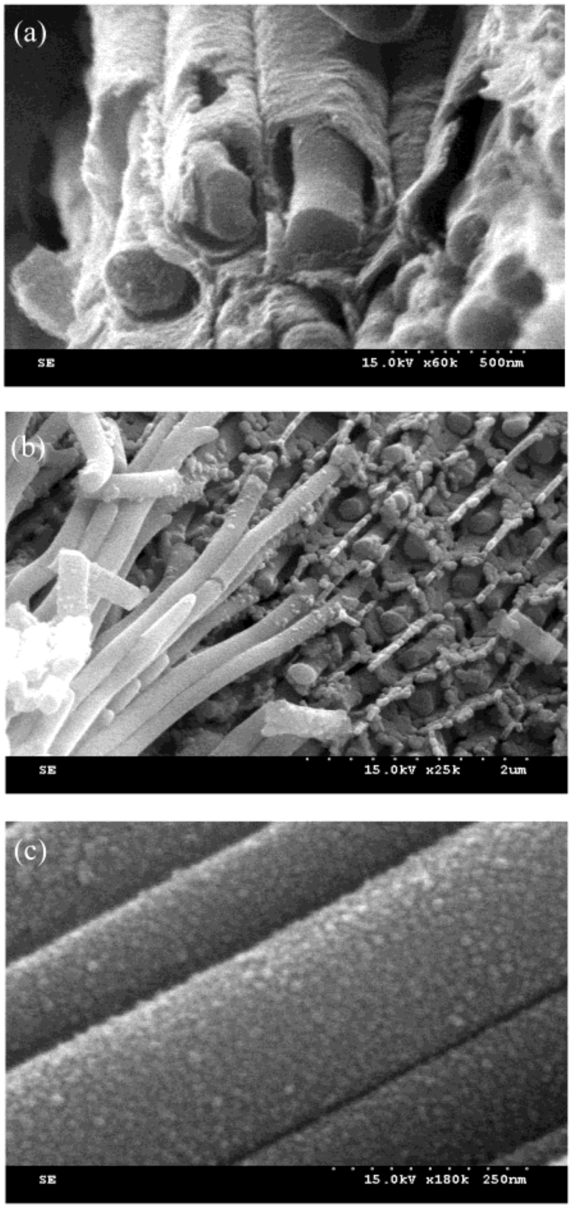

Figure 1. SEM images of TiO_2 nanostructures produced at 100 °C using AAM: (a) rods and tubules, (b) collective rods and crumbled tubules, and (c) magnified rods.

Some representative SEM images of TiO_2 nanostructures annealed at 100 °C are displayed in Figure 1a−c at different magnifications. Figure 1a shows tubules and rods of the whole nanostructure. The rods are encompassed by cylindrical tubules. The outer tubules appear to be smooth and the inner rods appear to be compact, or the tubules are more fragile than the rods. The tubule can be described as a single sheet of TiO_2 particles rolled into a cylinder, as its thickness is essentially the same as the size of the constituting particle, viz. about 60−80 nm. The rods are about 200−250 nm in diameter, whereas diameter of the tubules is about 500 nm, which far exceeds the average pore size (200 nm) of the AAM. This behavior is contrasted to the formation of TiO_2 from hydrolyzed TiF_4 solutions, where TiO_2 nanotubes or nanorods smaller than the pore size of AAM are formed.[8,11] Zhang and co-workers have also reported that the diameters of the nanorods correspond exactly to those of the templates.[9] It is also to be mentioned here that Zhang and coauthors have obtained much lesser diameters of TiO_2 nanowires than the pore size of alumina in their electrochemical fabrication of TiO_2 using nanochannel alumina.[12] Clusters, which are normally observed when particles are prepared from hydrolyzed $TiCl_4$ solution,[6] are not found on either the tubule walls or rod surface. Figure 1b additionally shows closely packed TiO_2 nanorods, which are straight, forming bundles. The magnified SEM image of the rods in Figure 1c shows that the rods consist of TiO_2 particles of about 20 nm, and have a much smoother surface than the tubules. We have observed that the diameters of the

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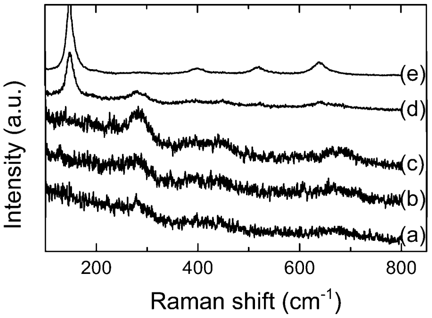

Figure 2. Raman spectra of TiO_2 nanomaterials produced at (a) room temperature, (b) 100 °C, (c) 200 °C, (d) 300 °C, and (e) 400 °C.

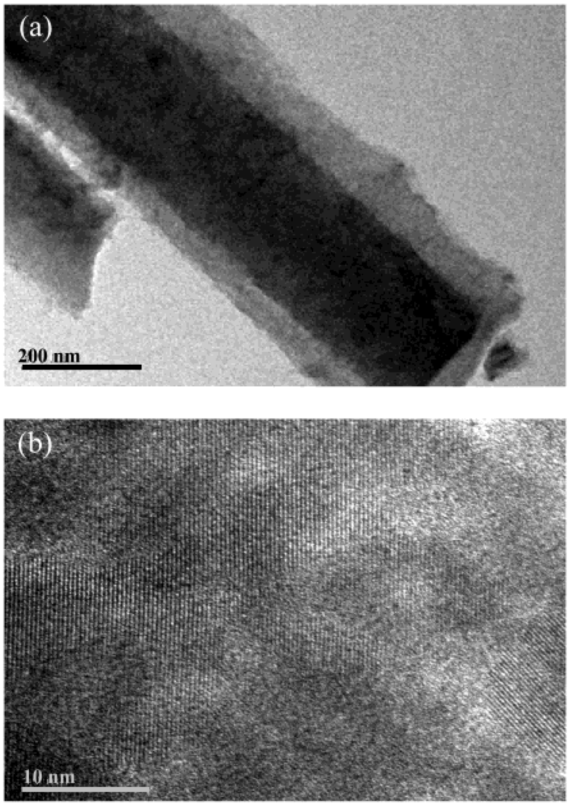

Figure 3. TEM photographs of TiO_2 prepared at 400 °C: (a) rod and tubule, and (b) a magnified portion of the tubule, showing the lattice fringes of the tubule edge.

rods are essentially independent of annealing temperature above 200 °C. This is because no organic polymers are used in the preparation step. The presence of such materials could have caused shrinkage in the rods during annealing.

Figure 2 shows Raman spectra of TiO_2 nanomaterials produced at several annealing temperatures for 2 h. The spectra are obtained with portions of the nanostructure consisting of both rod and tubule. We have also observed Raman spectra individually for tubule and rod and noted no other phase other than anatase. Before calcination TiO_2 is amorphous, as is expected. It can be seen that the intensities of the peaks increase at higher temperatures, indicating the increase of crystallinity of TiO_2 with temperature. Raman peaks at 144, 197, 400, and 516 cm^{-1} show that the AAM-$TiCl_4$-produced TiO_2 nanomaterial crystallizes as anatase. It is very interesting to note that irrespective of the precursor and solvent used for the preparation of TiO_2 its crystal phase is invariably anatase with template processes and in case of electrochemical deposition of the material.[3,9−13,18−23] This is true to the best of our knowledge. A broad band around 290 cm^{-1} is possibly originated from Ti−O−Na species, generated by NaOH treatment.[24,25] Supporting evidence regarding the nanostructure can be obtained from Figure 3a, where the low-magnification TEM photograph shows an open-end nanomaterial, produced at 400 °C, consisting of a rod clad in a tubule. The diameters of the rod and tubule are the same throughout the nanostructure and are consistent with those in the SEM shown in Figure 1. Figure 3b additionally shows a highly magnified TEM image of the tubule edge, indicating the crystalline lattice fringes of the tubule. The lattice fringes show that mostly the nearest layers in the tubule wall are separated by a plane distance of about 0.36 nm, which corresponds to the (101) plane of anatase phase.[8] It can be also noted that TiO_2 crystals are oriented in a random fashion, suggesting that there is no possibility of formation of multiwalls of the tubule, eliminating the possibility of layer-by-layer growth of the tubule on the inner surface of AAM.

On the basis of the results above, a possible mechanism for the formation of the nanomaterial is proposed. The unique structure of the nanomaterial indicates that the rods grow differently from the tubules. As hydrolyzed $TiCl_4$ solution becomes saturated with time at 50 °C within a pore, nucleation of polymeric Ti(IV) hydroxides for rods occurs homogeneously in the entire solution in the pore, leading to the formation of a large number of nuclei. The subsequent growth of these nuclei into particles in the AAM pore occurs presumably under the conditions of electrostatic repulsion between the positively charged surrounding alumina surface and the positively charged polymeric Ti(IV) hydroxides in the hydrolyzed $TiCl_4$ solution. This repulsive force tends to cause a higher concentration of polymeric Ti-nuclei at the central region of the pore with reference to the wall of the pore, while the counteranions get enriched in the space between the AAM wall and the central region. The higher concentration of Ti nuclei at the central region limits the size of the particles to be smaller. When smaller particles are interconnected upon annealing, a more compact rod is produced.

Unlike in the case of the rod formation, nucleation of polymeric Ti(IV) hydroxides for tubules occurs heterogeneously at the AAM surface where the interfacial energy is apparently low. The nucleation can be initiated during heating at 50 °C through hydrolysis by the formation of Ti−O−Al bonds between Ti(IV) complexes[16] such as $[Ti(OH_x)]^{(8-6x)-}$ and Al−OH sites on the pore wall.[11,26] After the initiation period, the nuclei can

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continue to grow by attracting more Ti(IV) complexes to form partly dehydrated, polymeric Ti(IV) hydroxide particles on the pore wall until the neighboring particles make contact with each other. At the same time, the AAM wall dissolves in the acidic solution of hydrolyzed $TiCl_4$. Note that the average diameter of the tubules is more than two times the average diameter of the pores, which is possible only with the dissolution of pore walls of the AAM in the acidic condition. The polymeric Ti(IV) hydroxide particles can continue attaching themselves onto the inside wall of the template during its dissolution through coordination bond formation. This view is reinforced by the report that TiO_2 sol particles adsorb to the AAM pore wall and their interaction accelerates the rate of gelation process.[11] The process would lead to the formation of a monolayer of TiO_2 particles in the form of a tubule. This is in consistency with the fact that the width of the tubule is the same as the particle size of TiO_2 in the tubule. The TiO_2 formed like this around the rods can be fragile because of the lack of support of AAM, which would have otherwise made it compact as in the case of the rod. The two-dimensional nature of the tubules compared to the three-dimensional nature of the rods can also be a reason for their fragile and compact natures, respectively.

The erosion of the AAM by acidic condition also is not expected to continue beyond a limit, as the acidity decreases after certain dissolution. The difference in the densities of tubule and rod and annealing of the nanostructure above 100 °C could cause the gap between the rod and tubule. The close contact of adjacent tubules in the SEM micrographs is consistent with the view that the membrane between them is eroded. NaOH treatment is, in any case, necessary for the complete dissolution of alumina membrane. Further investigation is necessary for better understanding of the formation of the TiO_2 nanostructure.

Conclusions

Electron microscopic and TEM analyses show that a TiO_2 nanostructure prepared in AAM consists of two distinct parts: encompassing fragile tubules and compact rods inside the tubules. Typically the tubules consist of TiO_2 particles of 60−80 nm diameter, whereas the rods are made up of about 20-nm TiO_2 particles. Diameter of the tubules far exceeds the average pore size of the AAM. The compact nature of the rod is understood to be due to the repulsive forces between the positively charged alumina surface and the positively charged polymeric Ti(IV) hydroxides in the hydrolyzed $TiCl_4$ solution. Lack of support of AAM is seen as the reason for the fragile nature of the tubule. The two-dimensional nature of the tubule compared to the three-dimensional nature of the rod can also be a reason for their fragility and compactness, respectively. The smaller and larger sizes of the particles of the rod and tubule, respectively, are attributed to their respective formation conditions. The small gap between the rod and the tubule could be due to the difference in their densities and also to the annealing of the nanostructure above 100 °C. Interestingly, and as seen in our case, it is noted that irrespective of the precursor and solvent used for the preparation of TiO_2 its crystal phase is invariably anatase with template processes and electrochemical deposition of the material.

Acknowledgment. This work is supported by the CRM-KOSEF, Korea.

CM030541Y

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