The effect of Sodium Concentrations on the Formation of Nanotubes Obtained from TiO_2

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The TiO_2 sol was prepared hydrothermally in an autoclave from aqueous $TiOCl_2$ solutions as a starting precursor. Hollow fibers were obtained when the sol-gel-derived TiO_2 sol was treated chemically with a NaOH solution and subsequently heated in the autoclave under various conditions. A systematic analysis of the influence of different NaOH concentrations on the formation of nanotubes was carried out. The details of the nanotubular structure were investigated by using transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray diffraction (XRD. From the TEM images, the outer and the inner diameters of the tubes were measured to be about 8 and 4 nm, respectively, the lengths were measured to be several hundreds of nanometers.

Keywords : TiO_2 sol, Titanate nanotubes, Hydrothermal process, Titania

1. INTRODUCTION

Nanotubes are ubiquitous in the world of science. Recently, a number of nanotubes, made of materials other than carbon, have attracted the attention of many inorganic chemists. Delving into the periodic table, these scientists are finding that nanotubes made from inorganic materials have intriguing properties quite different from those of their all-carbon cousins and a range of potential applications. Of such materials, titanates nanotubes have received a great deal of attention, in part because TiO_2 can exhibit a wealth of important photovoltaic (solar energy conversion), photocatalytic, semiconductor, catalytic support, and gas-sensing properties, especially when prepared in a nanomaterial. In addition, these materials can serve as low-voltage intercalation hosts for lithium and, hence, as cathodes for rechargeable lithium ion batteries or supercapacitors [1]. Research on TiO_2 includes nanoparticles [2], thin films [3], and mesoporous TiO_2 [4]. The titanium-oxide nanotubes are of particular interest because they have larger surface areas and higher photocatalytic activities [5]. TiO_2 tubes with diameters of 70-100 nm were produced using a sol-gel method [6] or porous alumina as a template [7]. Smaller nanotubes with diameters of about 8 nm were also reported, and the structure of the tube was confirmed to be anatase [8], anatase-rutile [9], or layered hydrogen titanate [10]. Following the discovery of nanotube morphology in carbon, a wide variety of layered materials have been shown to be able to form nanotubes [11]. However, the mechanism of formation and the method of regulating the morphologies (diameter and length, wall thickness, size distribution, and the sizes of nanotube agglomerates) of the various types of nanotubes are still the subject of intense research. Mainly, three approaches have been reported for the preparation of these tubular materials in powdery forms: the template method [12], the anodic oxidation method [13], and the wet chemical method [14]. The hydrothermal process, as a wet chemical method, has been used to obtain layered nanostructures.

In this paper, we report the synthesis of titanate nanotubes by using a chemical treatment of a TiO_2 sol with NaOH under hydrothermal conditions. We also make an attempt to see the effect of various NaOH concentrations, 2.5, 5.0, 7.5, 10.0, 15.0, and 20.0 M, on

the formation of these tubes.

2. EXPERIMENT

The process describing the preparation of TiO_2 precursor is thoroughly discussed in the literature [14]. To prepare the TiO_2 sol, we heated the TiO_2 precursor in an autoclave reactor (internal capacity of 500 ml) at 150 ^{0}C by applying pressure (N_2, 100 BAR) for 5 h. A small amount of the obtained TiO_2 sol was then chemically treated with various NaOH concentrations. After stirring, the resulting solution was transferred to a Ni-lined autoclave and was heated at 150 ^{0}C for 48 h. The obtained white product was washed with acid (0.1-N HCl), which involved stirring the sample in an acid solution, which was followed by a rinsing in deionized water until the solution showed a neutral pH. After filtration, the sample was subjected to a freeze-drying process at -57 ^{0}C to obtain the dried powder.
The characterization of these powders was carried out by employing different techniques, such as transmission electron microscopy (JEOL-2010), scanning electron microscopy (Hitachi S-4700), powder X-ray diffraction with Cu Kα radiation (Simens-D50050D).

3. RESULTS AND DISCUSSION

The crystalline qualities and the phase changes of different samples obtained after chemical treatment of the TiO_2 sol with various concentrations of NaOH under hydrothermal conditions was followed by employing XRD and SEM analysis techniques. The change in XRD patterns with NaOH concentration is shown in Fig. 1.
When the TiO_2 sol was treated with 2.5-M NaOH, a characteristic peak appeared at approximately $2\theta = 10$, which is thought to correspond to either $H_2Ti_3O_7$ or $H_2Ti_4O_9.H_2O$ [10], and the intensity of that peak increased with increasing NaOH concentration from 2.5 to 5.0 M and then began to decrease at higher concentrations. It is interesting to observe that, at a 5.0-M NaOH concentration (Fig. 1(c)), the intensity of the anatase peak at $2\theta = 25$ decreases and emergence of two new peaks takes place. On the basis of these patterns, it can be concluded that the formation of layered protonic titanates takes place, along with the persistence of the anatase phase, and a stage is reached in which anatase crytallinity is completely lost, which is followed by the generation of a new phase that may be ascribed to layered protonic titanates. A similar kind of XRD pattern (Fig. 1(d)) has been reported for titanate nanotubes [10].

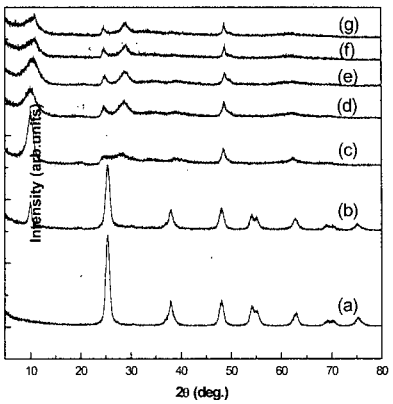

Fig. 1. Powder XRD patterns of different samples produced by hydrothermal treatment of a TiO_2 sol with various concentrations of NaOH at 150 ^{0}C for 48 h: (a) 0.0-M NaOH, (b) 2.5-M NaOH, (c) 5.0-M NaOH, (d) 7.5-M NaOH, (e) 10.0-M NaOH, (f) 15.0-M NaOH, and (g) 20.0-M NaOH.

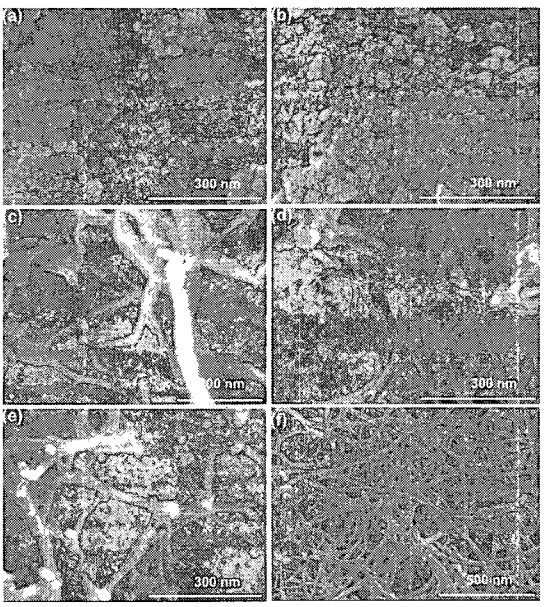

Fig. 2. SEM micrographs of different samples obtained by hydrothermal treatment of a TiO_2 sol with various concentrations of NaOH at 150 ^{0}C for 48 h: (a) 0.0-M NaOH, (b) 2.5-M NaOH, (c) 5.0-M NaOH, (d) 7.5-M NaOH, (e) 10.0-M NaOH, and (f) 15.0-M NaOH.

Fig. 2 shows the scanning electron micrographs (SEM) of the starting material and of the obtained powders treated with various concentrations of NaOH. The SEM analyses of different samples revealed that, at 2.5 M NaOH, no change was observed in the shapes of the nanoparticles of the TiO_2 sol, but as we increase the concentration of NaOH to 5.0 M (Fig. 2(c)), some parts of the TiO_2 sol were seen to be transformed into tubes and some parts into nanosheets or nanoplates. This pattern continued up to a 7.5-M NaOH concentration; i.e., the nanosheets/nanoplates were still observed along with the formation of nanotubes. However, these nanosheets disappeared completely when the concentration of NaOH was raised to 10.0 M (Fig. 2(e)). An increase in the number of nanotubes formed was observed with increasing NaOH concentration. A careful study revealed that the nanotubes formed above a 10.0-M NaOH concentration were longer and smaller in diameter than those obtained at other NaOH concentrations (Fig. 2(e)).

Fig. 3 illustrates transmission electron micrographs and a selected area electron diffraction pattern (SAED) of the obtained powder treated with a 10.0-M NaOH soution for 48 h at 150 ^{0}C. From the TEM images, the outer and the inner diameters of the tubes were measured to be about 8 and 4 nm, respectively, and the lengths were measured to be several hundreds of nanometers. All the nanotubes are open at both ends (Fig. 3(b)).

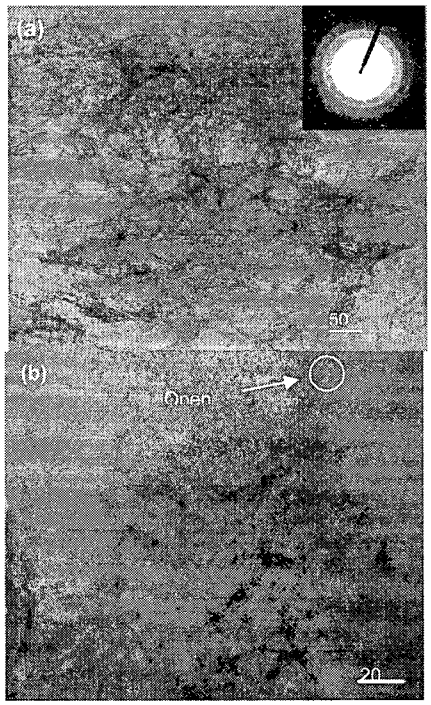

Fig. 3. Transmission electron micrographs (TEM) and selected area electron diffraction (SAED) pattern of the sample obtained by hydrothermal treatment of a TiO_2 sol with 10.0-M NaOH at 150 ^{0}C for 48 h: (a) shows the various lengths of nanotubes, and (b) shows the diameters and open ends of the nanotubes.

4. CONCLUSION

Titanate nanotubes were successfully obtained directly from a TiO_2 sol following a hydrothermal process in the presence of sodium hydroxide. The phase and morphology of these nanotubes as functions of the NaOH concentration were followed by using X-ray diffractometry and scanning electron microscopy, respectively. The formation of the nanotubes was found to increase with increasing NaOH concentrations. Transmission electron microscopy revealed that the outer diameter of the tubes was about 8 nm and the inner diameter was about 4 nm.

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