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A Review on Synthesis of Nano-TiO_2 via Different Methods

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Abstract

Titanium dioxide is one kind of important materials, which has been extensively investigated because of its unique electronic and optical properties. A large number of efforts have been made to synthesize TiO_2 materials with different methods. In this review paper, we summarize the synthesis pathways, morphology, as well as crystallization of the nanostructured TiO_2. In addition, we also mention several nanostructured TiO_2 materials.

1. Introduction

In the past decade, nanostructured materials have been of great interest as catalysts and other application because of their unique textural and structural characteristics. Much effort has concentrated on the important metal oxides such as TiO_2, SnO_2, VO_2, and ZnO. Titania is a very well-known and well-researched material due to the stability of its chemical structure, biocompatibility, physical, optical, and electrical properties. Its photocatalytic properties have been utilized in various environmental applications to remove contaminants from both water and air [1].

TiO_2 exists in three mineral forms: anatase, Rutile, and Brookite (Fig.1) [2]. Anatase type TiO_2 has a crystalline structure that corresponds to the tetragonal system (with dipyramidal habit) and is used mainly as a photocatalyst under UV irradiation. Rutile type TiO_2 also has a tetragonal crystal structure (with prismatic habit). This type of Titania is mainly used as white pigment in paint. Brookite type TiO_2 has an orthorhombic crystalline structure. TiO_2, therefore is a versatile material that has applications in various products such as paint pigments, sunscreen lotions, electrochemical electrodes, capacitors, solar cells, and even as a food coloring agent and in toothpastes [3]. In general, TiO_2 is preferred in anatase form because of its high photocatalytic activity, since it has a more negative conduction band edge potential (higher potential energy of photogenerated electrons), high specific area, non-toxic, photochemically stable and relatively inexpensive[4].

TiO_2 morphologies have mainly included nanostructures such as nanotubes [5], nanowires [6], nanorods [7], and mesoporous structures [8]. In recent years, a variety of synthesis methods such as hydrothermal method [9], solvothermal method [10], sol-gel method [11], direct oxidation method [12], chemical vapor deposition (CVD) [13], electrodeposition [14], sonochemical method [15], and microwave method [16] have been used for the preparation of TiO_2 nanostructured. This review focused on the different methods of synthesis and characterization of nanostructured TiO_2.

2. Synthetic Methods for TiO_2 Nanostructures

2.1. Hydrothermal Method

Hydrothermal synthesis is normally conducted in steel pressure vessels called autoclaves with or without Teflon liners under controlled temperature or pressure with the reaction in aqueous solutions. The temperature can be elevated above the boiling point of water, reaching the pressure of vapor saturation. The temperature and the amount of solution added to the autoclave largely determine the internal pressure produced. It is a method that is widely used for the production of small particles in the ceramics industry.

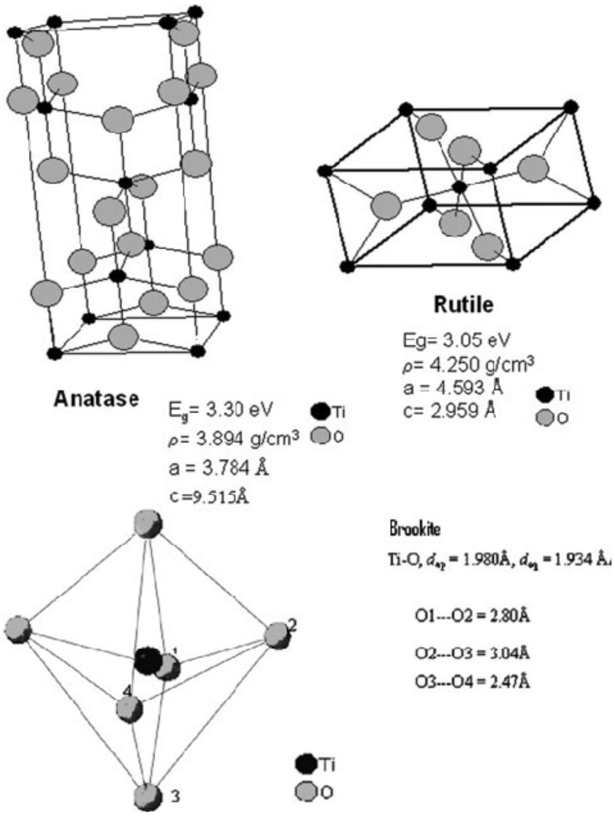

Fig. 1. Different forms of TiO_2 [4].

TiO_2 nanoparticles can be obtained by hydrothermal treatment of peptized precipitates of a titanium precursor with water [17]. The precipitates were prepared by adding a 0.5 M isopropanol solution of titanium butoxide into deionized water ($[H_2O]/[Ti]$) = 150), and then they were peptized at 70 °C for 1 h in the presence of tetraalkylammonium hydroxides. Typical TEM images of TiO_2 nanoparticles made with the hydrothermal method are shown in Fig. 2 [17].

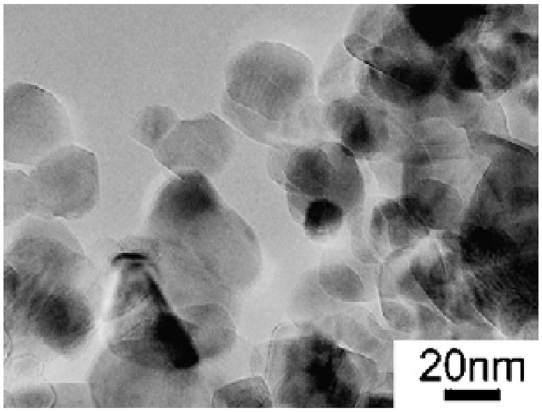

Fig. 2. TEM images of TiO_2 nanoparticles prepared by the hydrothermal method [17].

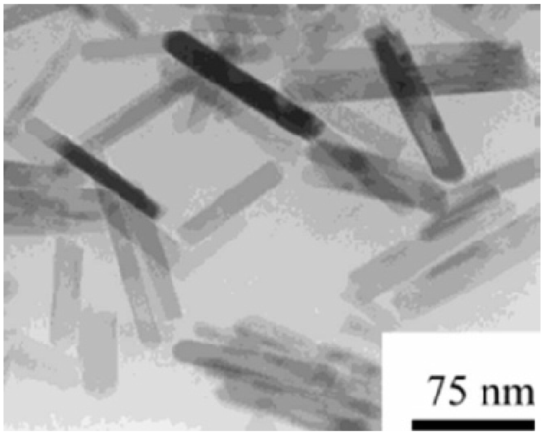

Fig. 3. TEM image of TiO_2 nanorods prepared with the hydrothermal method [18].

Besides TiO_2 nanoparticles, TiO_2 nanorods have also been synthesized with the hydrothermal method. Zhang et al. obtained TiO_2 nanorods by treating a dilute $TiCl_4$ solution at 333-423 °K for 12 h in the presence of acid or inorganic salts. Fig.3 shows a typical TEM image of the TiO_2 nanorods prepared with the hydrothermal method. Fig.4 shows the SEM images of TiO_2 nanowires [18-21].

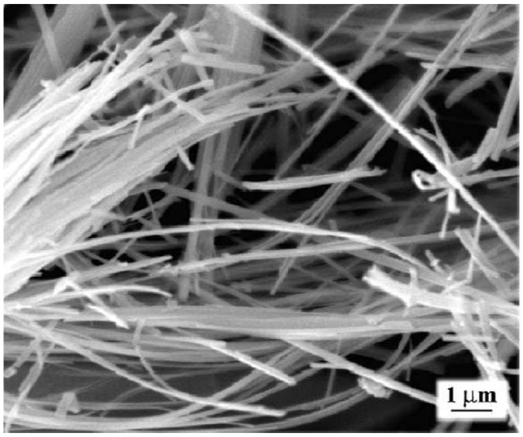

Fig. 4. SEM images of TiO_2 nanowires prepared with the hydrothermal method [21].

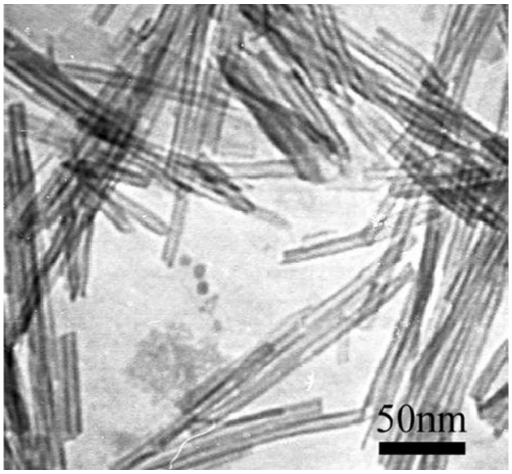

Fig. 5. TEM images of TiO_2 nanotubes prepared with the hydrothermal method [22].

TiO_2 nanotubes have also been synthesized with the hydrothermal method. In a typical preparation procedure, 2 g P25 TiO_2 white power was placed into a Teflon-lined autoclave of 100 ml capacity. Then, the autoclave was filled with 80 ml of 10 M NaOH aqueous solution, sealed into a stainless tank and maintained at 130 °C for 24 h. After the autoclave was naturally cooled to room temperature, the obtained sample was filtered, washed with distilled water for several times. Then, the obtained products were collected and washed with HCl aqueous solution (pH 1.6) for 24 h, and washed with distilled water for several times until the pH value turned to 7. At last, the products were annealed at 400 °C in air for 2h. Fig. 5 shows a typical TEM image of the TiO_2 nanotubes prepared with the hydrothermal method [22].

2.2. Solvothermal Method

The solvothermal method is almost identical to the hydrothermal method except that the solvent used here is nonaqueous. However, the temperature can be elevated much higher than that in hydrothermal method, since a variety of organic solvents with high boiling points can be chosen. The solvothermal method normally has better control than hydrothermal methods of the size and shape distributions and the crystallinity of the TiO_2 nanoparticles. The solvothermal method has been found to be a versatile method for the synthesis of a variety of nanoparticles with narrow size distribution and dispersity. The solvothermal method has been employed to synthesize TiO_2 nanoparticles [23-25]. Fig.6 show a typical TEM image of the TiO_2 nanoparticles prepared with the solvothermal method.

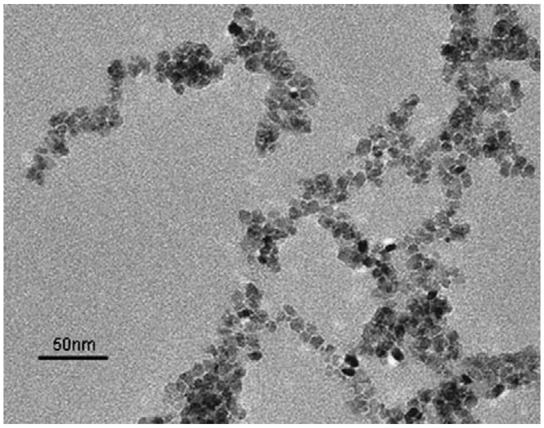

Fig.6. TEM images of TiO_2 nanoparticles prepared with the hydrothermal method [23].

2.3. Sol-Gel Method

The sol-gel method is a versatile process used in making various ceramic materials. In a typical sol-gel process, a colloidal suspension, or a sol, is formed from the hydrolysis and polymerization reactions of the precursors, which are usually inorganic metal salts or metal organic compounds such as metal alkoxides. Complete polymerization and loss of solvent leads to the transition from the liquid sol into a solid gel phase. Thin films can be produced on a piece of substrate by spin-coating or dip-coating. A wet gel will form when the sol is cast into a mold, and the wet gel is converted into a dense ceramic with further drying and heat treatment. A highly porous and extremely low-density material called an aerogel is obtained if the solvent in a wet gel is removed under a supercritical condition. Ceramic fibers can be drawn from the sol when the viscosity of a sol is adjusted into a proper viscosity range. Ultrafine and uniform ceramic powders are formed by precipitation, spray pyrolysis, or emulsion techniques. Under proper conditions, nanomaterials can be obtained.

Nanostructured TiO_2 has been synthesized with the sol-gel method from hydrolysis of a titanium precursor. This process normally proceeds via an acid-catalyzed hydrolysis step of titanium (IV) alkoxide followed by condensation. The development of Ti-O-Ti chains is favored with low content of water, low hydrolysis rates, and excess titanium alkoxide in the reaction mixture. Three dimensional polymeric skeletons with close packing result from the development of Ti-O-Ti chains. The formation of $Ti(OH)_4$ is favored with high hydrolysis rates for a medium amount of water. The presence of a large quantity of Ti-OH and insufficient development of three-dimensional polymeric skeletons lead to loosely packed first-order particles. Polymeric Ti-O-Ti chains are developed in the presence of a large excess of water. Closely packed first order particles are yielded via a three-dimensionally developed gel skeleton.

Highly crystalline anatase TiO_2 nanoparticles with different sizes and shapes could be obtained with the polycondensation of titanium alkoxide in the presence of tetramethylammonium hydroxide [26, 27]. Fig.7 shows the TEM images of TiO_2 nanoparticles prepared by sol-gel method.

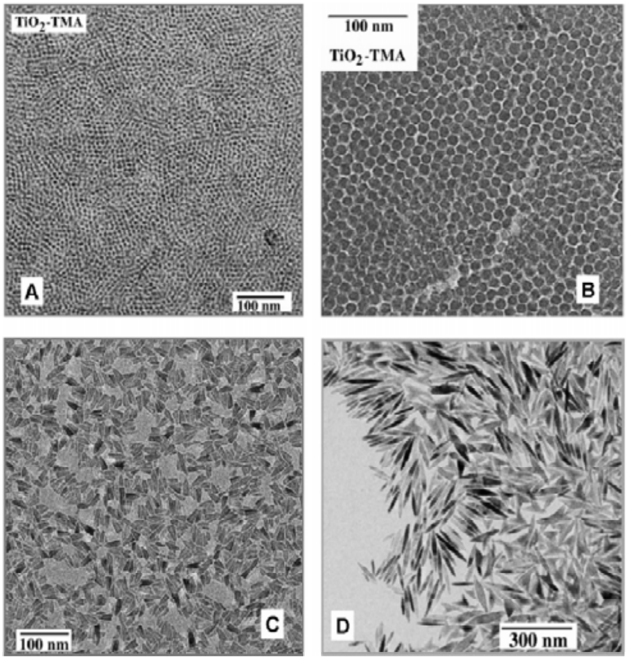

Fig. 7. TEM images of TiO_2 nanoparticles prepared by hydrolysis of $Ti(OR)_4$ in the presence of tetramethylammonium hydroxide [26].

2.4. Direct Oxidation Method

Nanostructured TiO_2 can be obtained by oxidation of titanium metal using oxidants or under anodization. Crystalline TiO_2 nanorods have been obtained by direct oxidation of a titanium metal plate with hydrogen peroxide [28-30]. Typically, TiO_2 nanorods on a Ti plate are obtained when a cleaned Ti plate is put in 50 mL of a 30 wt% H_2O_2 solution at 353 $^{\circ}$K for 72 h. The formation of crystalline TiO_2 occurs through a dissolution precipitation mechanism. By the addition of inorganic salts of NaX (X = F^-, Cl^-, and SO_4^{2-}), the crystalline phase of TiO_2 nanorods can be controlled. The addition of F^- and SO_4^{2-} helps the formation of pure anatase, while the addition of Cl^- favors the formation of rutile. Fig.8 shows a typical SEM image of TiO_2 nanorods prepared with this method [28].

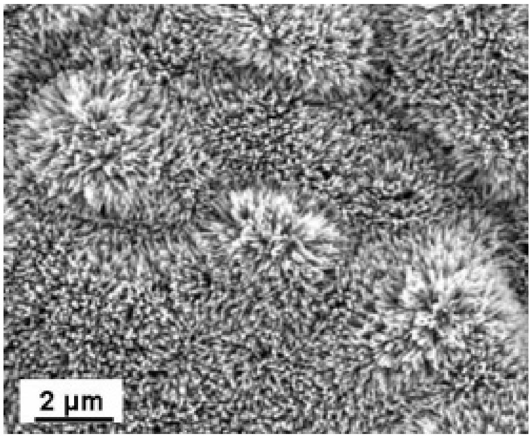

Fig. 8. SEM morphology of TiO_2 nanorods by directly oxidizing a Ti plate with a H_2O_2 solution [28].

TiO_2 nanotubes can also be obtained by oxidation of titanium metal under anodization. For example, a commercially pure Ti foil 0.05 mm thick was degreased with acetone followed by rinsing with deionized water and drying. For anodizing, we used Ti sample with the exposure area of 1 cm^2 as a working electrode and Pt plate as a counter electrode. Anodizing was performed in solutions of 0.5 wt% NH_4F and x M malonic acid (x = 0.2) by varying anodizing time from 1 min to 6 h. Voltages from 5 V to 20 V were applied on the specimen using DC power supply, and the corresponding current was recorded using an attached digital multimeter. All anodizing experiments were conducted at an ambient temperature (22±2 $^{\circ}$C) [12].

The surface and cross-sectional morphologies of the TiO_2 nanotube were analyzed using scanning electron microscope (SEM) (Fig. 9).

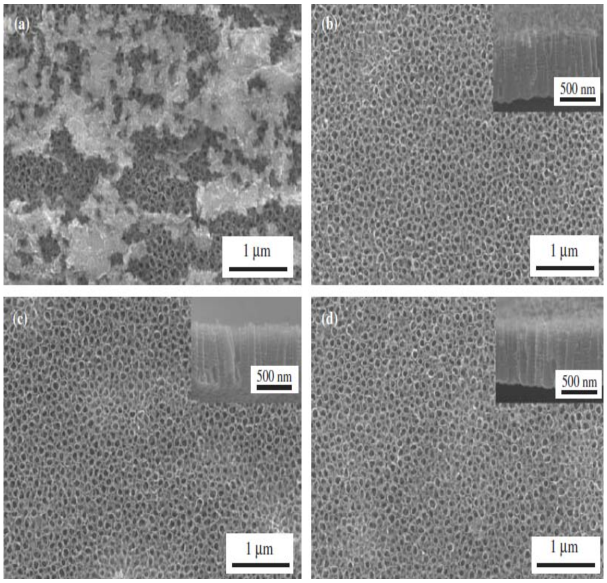

Fig. 9. Surface and cross-sectional morphologies of TiO_2 nanotubes obtained from anodizing Ti for 1 h at 20 V in solutions of 0.5 wt% NH_4F and x M malonic acid; (a) 0 M, (b) 0.1 M, (c) 1 M and (d) 2 M [12].

2.5. Chemical Vapor Deposition

Vapor deposition refers to any process in which materials in a vapor state are condensed to form a solid-phase material. These processes are normally used to form coatings to alter the mechanical, electrical, thermal, optical, corrosion resistance, and wear resistance properties of various substrates. In CVD processes, thermal energy heats the gases in the coating chamber and drives the deposition reaction. In CVD, flow rate, gas composition, deposition temperature, pressure and deposition chamber geometry are the process parameters by which deposition can be controlled to have nanoforms of the desired material.

Djerdja et al. [31] reported nanocrystalline TiO_2 films by CVD on different substrates at relatively low temperature of 320 °C using $TiCl_4$ as a precursor and found that the nature of substrates influence the size and distribution of nanograins in the films. Byun et al. prepared TiO_2 thin films at 287–362 °C using titanium (IV) tetraisopropoxide (TTIP) precursor and O_2 gas [32]. Fig.10 shows a schematic diagram of the experimental setup of chemical vapor deposition.

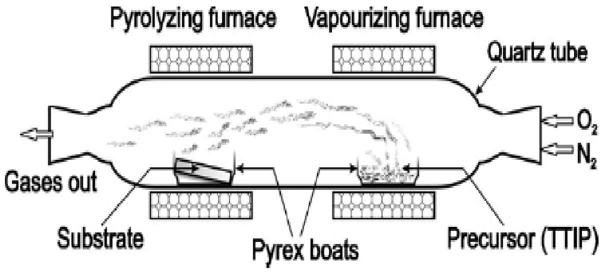

Fig. 10. Schematic diagram of the CVD apparatus. N_2 as carrier gas and O_2 as reactant gas [13].

Fig. 11 shows the typical XRD pattern of TiO_2 film (grown on glass substrate at 400 °C) recorded in the diffraction angle range of 10–100 °C. The matching of the observed and standard values confirms that the deposited films are of phase-pure anatase TiO_2 with tetragonal structure. [33]. The crystallite size of 10 ± 2 nm was determined by the broadening of the (101) diffraction peak at 25.35 °C, using a well-known Scherrer's formula [34].

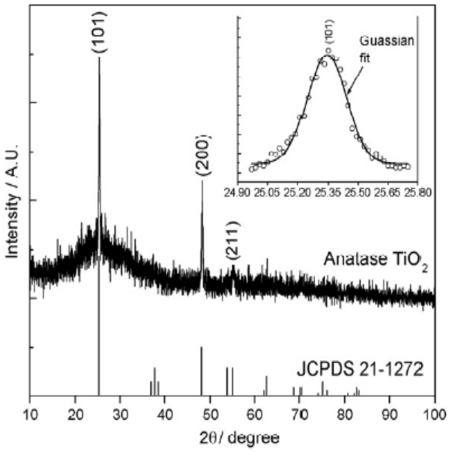

Fig. 11. X-ray diffraction spectra of chemical vapor deposited anatase TiO_2 thin films [13, 33].

2.6. Electrodeposition

Electrodeposition is commonly employed to produce a coating, usually metallic, on a surface by the action of reduction at the cathode. The substrate to be coated is used as cathode and immersed into a solution which contains a salt of the metal to be deposited. The metallic ions are attracted to the cathode and reduced to metallic form.

With the use of the template of an anodic alumina membrane (AAM), TiO_2 nanowires can be obtained by electrodeposition [35, 36]. In a typical process, the electrodeposition is carried out in 0.2 M $TiCl_3$ solution with pH= 2 with a pulsed electrodeposition approach, and titanium and/or its compound are deposited into the pores of the AAM. By heating the above deposited template at 500 °C for 4 h and removing the template, pure anatase TiO_2 nanowires can be obtained. Fig.12 shows a representative SEM image of TiO_2 nanowires [36].

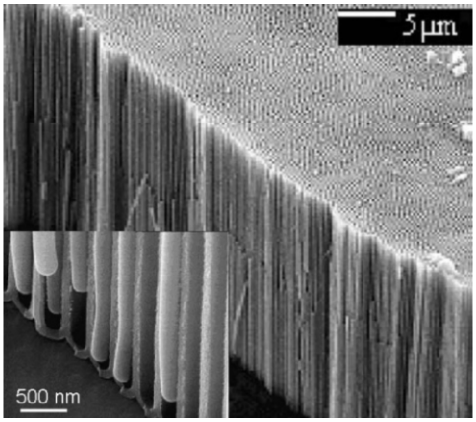

Fig. 12. Cross-sectional SEM image of TiO_2 nanowires electrodeposited in AAM pores [36].

2.7. Sonochemical Method

Ultrasound has been very useful in the synthesis of a wide range of nanostructured materials, including high-surface area transition metals, alloys, carbides, oxides, and colloids. The chemical effects of ultrasound do not come from a direct interaction with molecular species. Instead, sonochemistry arises from acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid.

In a typical procedure for preparation of TiO_2 nanoparticles, 0.5 g TiO_2 pellets were dissolved into 30 ml NaOH solution (10 M) under vigorous stirring at room temperature for 2 h. Then the yellowish solution was irradiated in an ultrasonic bath (Power Sonic 405, 40 kHz and 350 W) for 2h in ambient temperature. The resultant precipitates were then centrifuged, washed and decanted with deionized water several times and dried at 60 °C for 24 h [15].

Zhu et al. developed Titania whiskers and nanotubes with the assistance of sonication as shown in Fig. 13 [37].

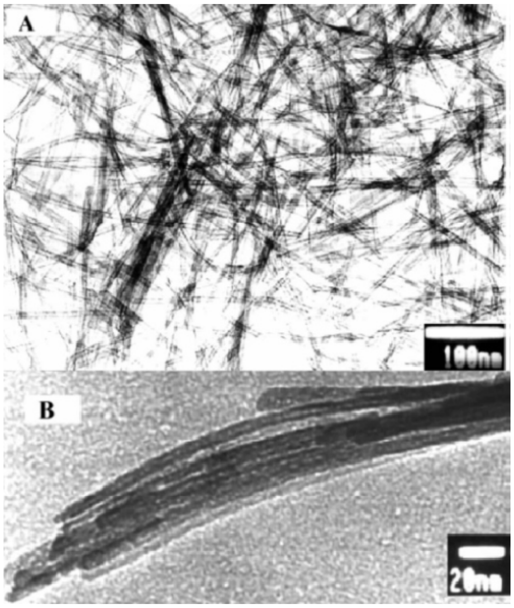

Fig. 13. TEM images of TiO_2 nanotubes (A) and nanowhiskers (B) prepared with the sonochemical method [37].

2.8. Microwave Method

A dielectric material can be processed with energy in the form of high-frequency electromagnetic waves. The principal frequencies of microwave heating are between 900 and 2450

MHz. At lower microwave frequencies, conductive currents flowing within the material due to the movement of ionic constituents can transfer energy from the microwave field to the material. At higher frequencies, the energy absorption is primarily due to molecules with a permanent dipole which tend to reorientate under the influence of a microwave electric field.

Microwave radiation is applied to prepare various TiO_2 nanostructured [16, 38-40]. For example, TiO_2 synthesis has been realized by forced hydrolysis in hydrothermal condition starting from a 0.5 M solution of $TiOCl_2$ with the employment of both a conventional and a microwave thermal treatment. The microwave-assisted syntheses have been conducted by using a microwave digestion system. The system uses 2.45 GHz microwaves and is controlled by both temperature and pressure (P_{max}=14 atm). According to literature data [41], microwave-hydrothermal treatments are conducted at 195°C for different times ranging from 5 min to 1 h. The time, pressure/temperature, and power have been computer controlled. The conventional synthesis was conducted at the same temperature for time ranging from 1 to 32 h in an electric oven using bombs with metal bodies and removable PTFE liners. After both synthesis reactions, the obtained suspensions, which present a pH ranging from 0.9 to 1, were repeatedly washed with distillated H_2O to eliminate chloride ions, and successively with NaOH 0.1N to neutralize the excess acidity. The suspensions were then centrifuged and dried in an oven at 110 °C [16].

Wu et al. synthesized TiO_2 nanotubes by microwave radiation via the reaction of TiO_2 crystals of anatase, rutile, or mixed phase and NaOH aqueous solution under a certain microwave power [42]. Fig.14 shows a typical SEM image of TiO_2 nanotubes prepared with this method [43].

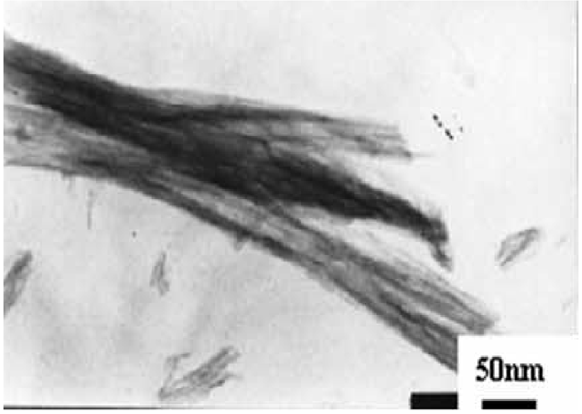

Fig. 14. TEM images of TiO_2 nanotubes prepared with the microwave method [43].

3. Conclusion

In this review, we summarize the progress in the synthesis nanostructured TiO_2. In the recent years, the tremendous effort put into nanostructured TiO_2 has resulted in a rich database for their synthesis, properties, modifications, and applications. The continuing progresses in the synthesis and modifications of nanostructured TiO_2 have brought new properties and new applications with improved performance. Accompanied by the progress in the synthesis of TiO_2 nanostructured are new findings in the synthesis of TiO_2 nanorods, nanotubes, nanowires, as well as mesoporous structures. Since the industrial production of the nanostructured TiO_2 has not been realized yet, large scale preparation method should be developed.

Acknowledgment

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