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Influence of autogeneous pressure under hydrothermal reaction on the structural and thermal stability of nanostructured titanates

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Abstract

Synthesis of four different morphologies of nanostructured titanates (sphere (TNS), sponge (TNSp), tube (TNT) and wire (TNW)) by hydrothermal reaction was investigated under the presence/absence of autogeneous pressure. Starting from 5 m^2/g anatase TiO_2 particles (com–TiO_2), TNS and TNSp products with surface area > 200 m^2/g were obtained under atmospheric pressure at 150 and 200 °C, respectively. On the other hand, TNT (192 m^2/g) and TNW (23 m^2/g) were synthesized at 150 and 200 °C under autogeneous pressure in a Teflon line autoclave reactor, respectively. After annealing at 600 °C, TNS, TNSp, and TNT transformed back into anatase TiO_2 but their surface areas were still much higher than the original one (60–70 m^2/g). Annealing of the TNW resulted in metastable form TiO_2 under similar conditions with no significant change of the surface area.

Keywords: Hydrothermal; Titanate; Nanotube; Nanowire

1. Introduction

Owing to their enhanced specific surface area, mesopore volume, and cation-exchange capacity, nanostructured TiO_2 materials has been explored in several fields, such as catalysis, biochemistry, separation science, and sensors [1–7]. Since the innovative work of Kasuga et al. [8], who first synthesized uniform titanate nanotubes by hydrothermal reaction of crystalline TiO_2 in highly concentrated NaOH solution, many attempts have been made to elucidate the mechanism of this synthesis route and the factors determining the composition, crystal and textural structure of the resulting nanostructured materials [9,10]. Typically, four different morphologies of titanates were observed during alkaline hydrothermal treatment of TiO_2 including nanotubes (I), nanosheets (II), nanorods or nanowires (III), and nanofibers, nanoribbons, or nanobelts (IV). It has been suggested that under alkaline conditions, the observed intermediate single layer and multi-layered titanates nanosheets play a key role in the formation of tubular morphology [11,12]. These nanosheets can scroll or fold into a nanotubular morphology. The driving force for curving these nanotubes has been considered by many groups. For examples, Zhang et al. [13] proposed a bending mechanism due to an asymmetrical chemical environment from the imbalance of H^+ or Na^+ ion concentration on two different sides of a nanosheet. Another reason for bending multilayered nanosheets is that mechanical tensions arise during the process of dissolution/crystallization in nanosheets [12].

Several parameters have been investigated, such as reaction time, reaction temperature, concentration of NaOH, average size of raw TiO_2 powder, post-synthesis heat-treatment temperature, and sonication pretreatment power [14–27], to find out their effects on morphology transformation, specific surface area, crystal structure, and so on. However, in those previous studies, the hydrothermal reaction occurred under autogeneous pressure. The morphology and structural properties of the nanostructured titanates formed in the absence of autogeneous pressure have seldom been reported.

In the present work, the synthesis of nanostructured titanates was carried out under the presence/absence of autogeneous pressure. Unlike the typical titanate nanotubes and nanowires, different titanate morphology such as nanosphere and sponge

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can be obtained when TiO_2 was treated in NaOH without autogeneous pressure. Physical properties and thermal stability of these nanostructure titanates were investigated using X-ray diffraction (XRD), N_2 physisorption, scanning electron microscope (SEM), and transmission electron microscopy (TEM).

2. Experimental

2.1. Powder synthesis

Synthesis of nanostructured titanates was carried out by the hydrothermal method using anatase TiO_2 (Com–TiO_2, Sigma-Aldrich) as the starting material. First, 1.5 g of TiO_2 powder was suspended in 40 ml of 10 M NaOH and then the mixture was sonicated for 10 min. Then, the mixture was transferred to a flask or Teflon-lined stanless steel autoclave, and heated at various reaction temperatures ranging from 150 to 200 °C for 24 h in an oven. After hydrothermal reaction, the autoclave was cooled to room temperature by natural cool down. The sample was washed with 0.1 M HCl for several times followed by deionized water until pH value approached that of the deionized water. Finally, the sample was dried at 110 °C for 24 h. The dried powder was annealed at 400, 500, and 600 °C for 1 h in air.

2.2. Powder characterization

XRD patterns were determined using a Siemens D5000 X-ray diffractometer using a Ni filtered CuK_α radiation. The morphology and particle size were obtained using a Hitachi s-3400N scanning electron microscope and a JEOL-JEM 2010 transmission electron microscope. Specific surface area of the sample was measured by nitrogen gas adsorption at liquid nitrogen temperature (-196 °C) using a Micromeritics Chemi-Sorb 2750 system.

3. Results and discussion

The SEM micrographs of the as-synthesized powder are shown in Fig. 1. In the absence of autogeneous pressure, spherical shape particles (TNS) were formed after treatment at 150 °C. Further increasing hydrothermal temperature to 200 °C, sponge-like particles (TNSp) were obtained instead. On the other hand, hydrothermal treatment under autogeneous pressure, the as-synthesized sample showed fiber-like morphology. The length of the nanofibers formed at 150 °C was varied ranging from several 10 μm to more than 100 μm. Increasing hydrothermal temperature to 200 °C, the diameters of nanofibers were increased and the lengths became shorten. The TEM experiments were carried in order to investigate the true structure of these nanofibers (solid or hollow) and the results are shown in Fig. 2. The starting anatase TiO_2 (Com–TiO_2) consisted of predominately spherical particles with average size around 100–200 nm. Moreover, the spherical TNS were in fact consisted of the agglomeration of nano-sized particles. The as-synthesized nanofibers formed at 150 °C were hollow with the outer and inner diameter of the nanotubes (TNT) of approximately 10–12 nm and 4–6 nm, respectively. Increasing temperature to 200 °C led to the transformation of nanotubes to nanowire (TNW) with non-hollow morphology with a length of several micrometers and width varied between 60–100 nm. These results are in good agreement with the SEM images.

Fig. 3 shows the XRD patterns of the starting anatase TiO_2 and the as-synthesized particles. The XRD patterns of all the hydrothermal-made products show the characteristic peaks of titanates with two main peaks at 2θ degrees 24.5° and 48.5° corresponding to the reflection (100) and (200) plane of H-titanate $H_2Ti_xO_{2x+1}$, probably trititanate ($H_2Ti_3O_7$) [28]. No diffraction peaks of other impurities (such as starting anatase TiO_2 and NaCl) were observed.

From the above results, the formation mechanism of nanostructure titante is different between the reaction systems with and without autogeneous pressure. Several researchers have studied the mechanism of the hydrothermal reaction between raw TiO_2 and NaOH solution to form titanate nanostructure using both theoretical and experimental methods. There is a general agreement that the reaction proceeds through several stages [29–31], including the slow dissolution of raw TiO_2 in NaOH solution accompanied by epitaxial growth of layered nanosheets of sodium titanates followed by the rolling up of exfoliated titanate sheets to form nanotube or nanorod samples. The driving force for the scrolling of the nanosheets into nanotubes has been proposed by Zhang et al. [4] including asymmetrical chemical environment on the two opposite sides of the nanosheet or the internal stress arising in the multilayered nanosheets from an imbalance in width, which occurred during the crystallization. Further increasing of reaction temperature resulted in the formation of nanorod structures due to the decreasing of nucleation and preferential crystal growth along the 010 direction of trititanate. However, this was probably not the case for the hydrothermal treatment without autogeneous pressure since there was a change in the nanostructure. It would start from the reaction between anatase TiO_2 and NaOH solution where the small spherical particles of titanates were formed and aggregated to form larger particles with an equivalent size of the raw TiO_2. It seemed to be that the reaction took place on the surface of TiO_2 to form small spherical particles and penetrate deep down inside the particles by diffusion. When the reaction temperature increased the sponge particles were formed. The reaction pathway to form nanostructure titanate under different conditions (with and without autogeneous pressure) is summarized in Scheme 1.

3.1. Thermal stability of nanostructure titnates

Another difficulty while utilizing nanostructure titanates is that the nanotubular structure of titanates is relatively unstable and can undergo further phase transformation upon heating, [27] acid treatment, [28] or other chemical treatments, during or after preparation of nanotubes. Thermal stability of the nanostructure titanate was investigated by calcining the as-synthesized product

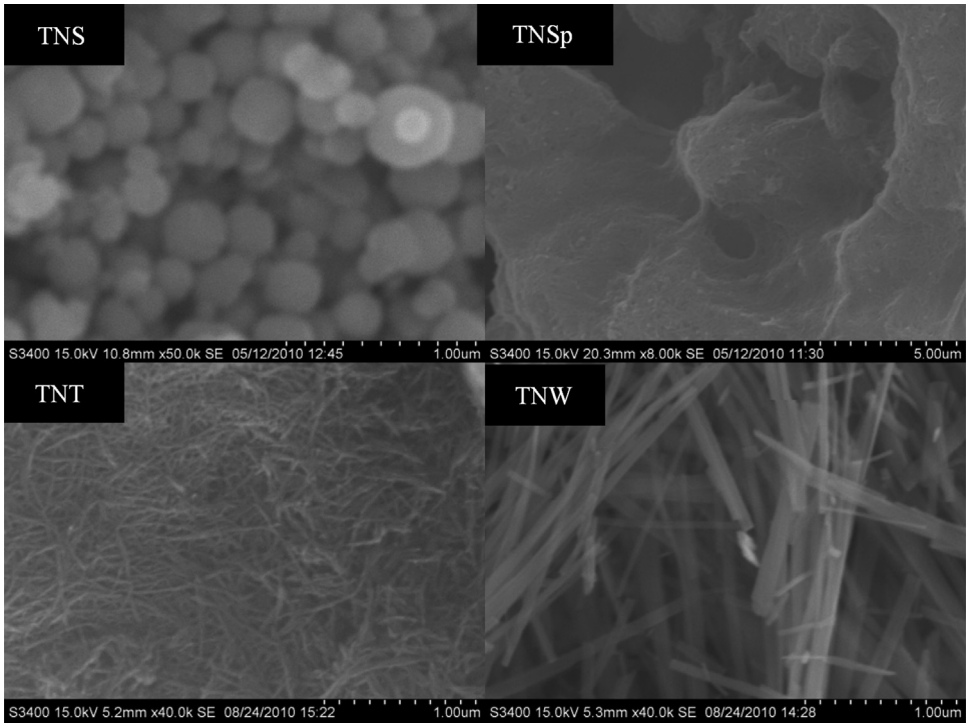


Fig. 1. SEM micrographs of the nanostructure titanate.

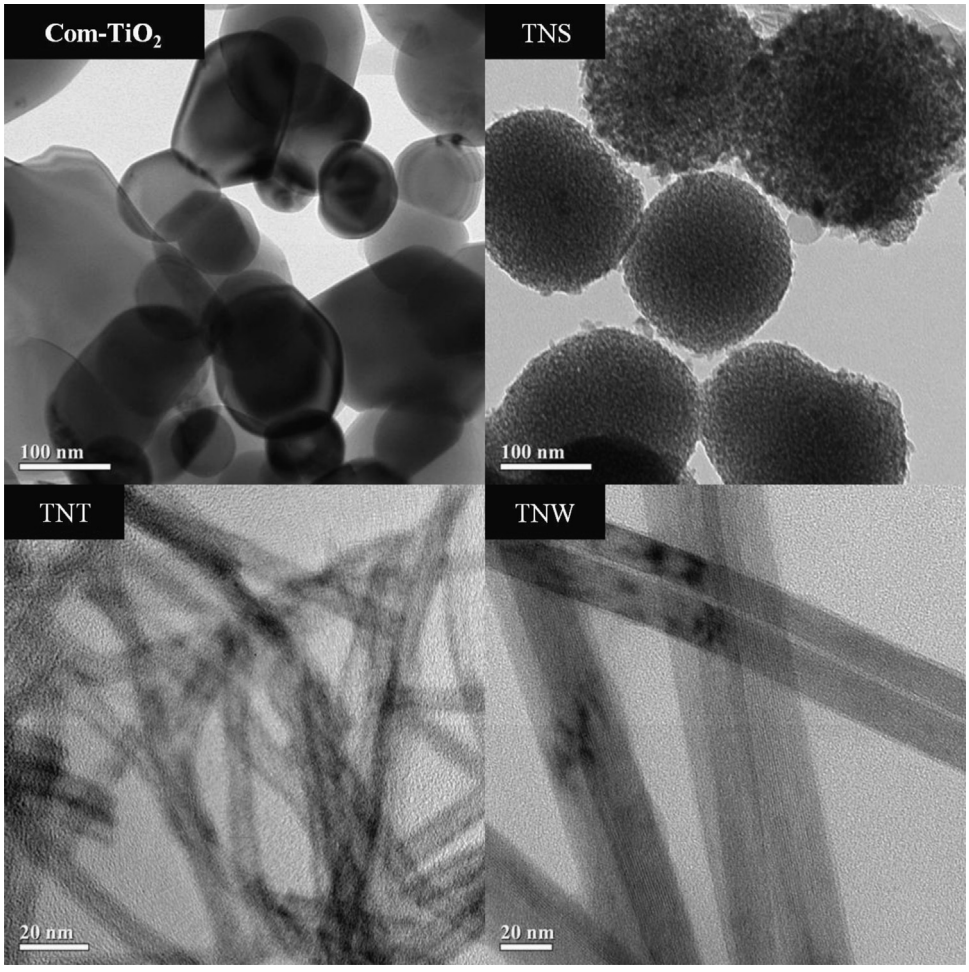


Fig. 2. TEM micrographs of the commercial TiO_2 and nanostructure titanate.

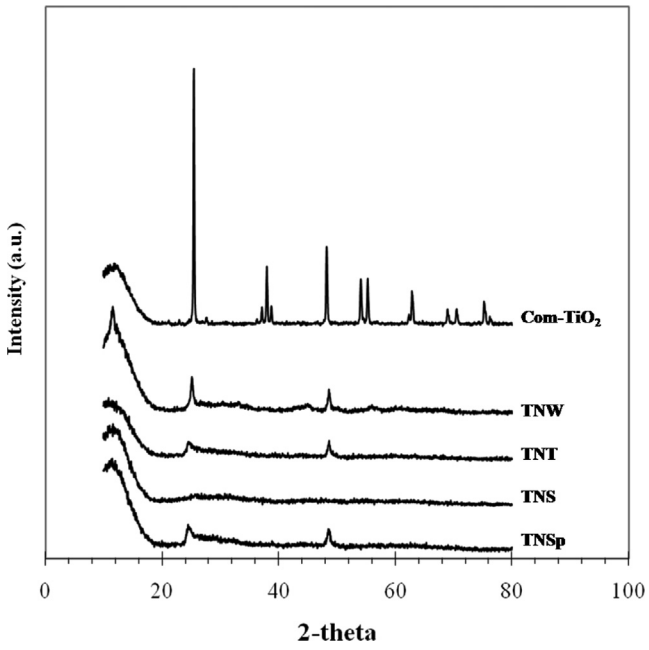
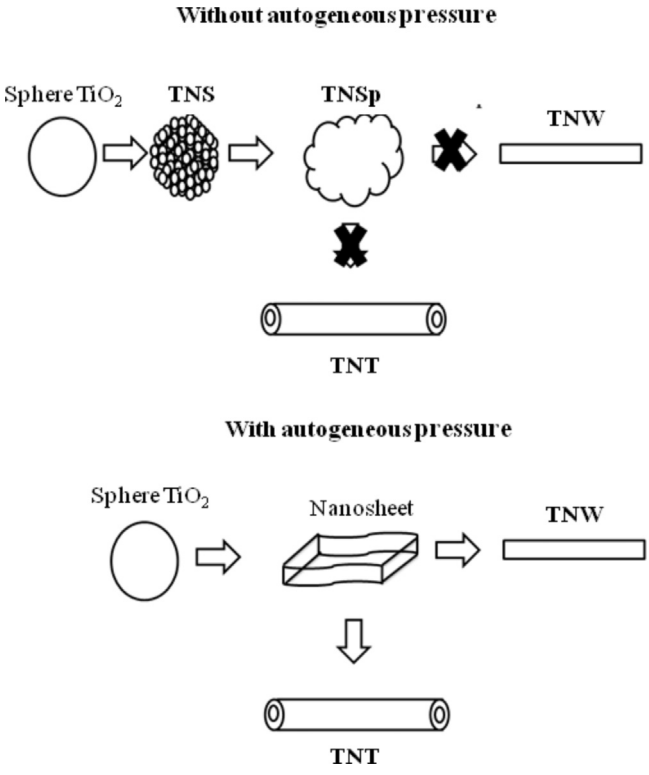


Fig. 3. XRD patterns of the commercial TiO_2.



Scheme 1. Titante formation mechanism.

at various temperatures for 1 h. Fig. 4 shows the XRD patterns of the nanostructure titanates (sphere, sponge, tube, and rod) after annealing at 400–600 °C. The as-prepared powder exhibited poor crystalline quality. The crystalline structure of the sample was improved by thermal treatment. According to the XRD results, annealing spherical-shape, sponge-like, and nanotube titanate at 400 °C resulted in the formation of anatase TiO_2 phase. When the sample was annealed at 500 °C and 600 °C, the peak intensities corresponding to anatase TiO_2 increased and the characteristic peaks of titanate disappeared. In other words, the titanate was completely transformed back to anatase TiO_2. For the titanate nanowires, after annealing at the temperature in the range of 400–600 °C, a metastable form of titanium dioxide was observed as shown in Fig. 4. It is suggested that the titanate nanowires were completely dehydrated and re-crystallized into metastable TiO_2 (TiO_2–B) [32]. Further increasing of the annealing temperature to 700 °C, the XRD pattern of anatase TiO_2 was observed (the results not shown). This indicates that metastable TiO_2 (TiO_2–B) was transformed to anatase TiO_2 at higher temperature.

The SEM images of the titanate nanostructure annealed at 600 °C are shown in Fig. 5. It can be seen that the morphologies of TNS and TNSp were not changed while TNT particles were shorter than the as-synthesized ones and some of them were converted to particles because the tubular structure was collapsed when annealed at relatively high temperature [31]. It should also be noted that the nanotube structure was not formed by annealing of the nanosheet or nanotube particles. This result suggests that the formation of the nanotube structure occurs under the reaction conditions with autogeneous pressure. TNW particles became larger due to the sintering process.

Fig. 6 illustrates the TEM images of annealed TNT and TNW. After thermal treatment at 600 °C, the nanotubes were partially broken and the hollow disappeared. The rod-like and some particles structure were observed. This is consistent to those previously reported regarding the conversion of the titanates into anatase TiO_2 phase by thermal dehydration [33,34]. This is associated with the collapse of the interlayer spacing between the walls of the nanotubes, resulting in the anatase phase as confirmed by the XRD results. Therefore, it can be concluded that during annealing treatment at high temperature, the chemical bond such as H_2O and –OH were removed from the titanate nanotubes so that then it converted back to particles again. For TNW, the morphology was not significant changed after thermal treatment at 600 °C.

Specific surface areas of the samples were determined from the N_2 physisorption data using Brunauer–Emmett–Teller (BET) technique. Table 1 summarizes the BET surface area of all the titanates before and after calcination at 600 °C. The BET surface area of the Com–TiO_2 as the starting material was 5 m^2/g. Hydrothermal treatment under atmospheric pressure at 150 °C resulted in a dramatically increased BET surface area to 211 m^2/g whereas the samples treated under autogeneous pressure exhibited the BET surface area of 192 m^2/g. Increasing of the BET surface areas was attributed to the morphology change to the nanostructure tianates that possessed higher surface area. The sample synthesized at 200 °C under autogeneous pressure had the lowest BET surface area (23.2 m^2/g) due to non-hollow structure of the TNW. After calcination at 600 °C, TNS, TNSp, and TNW transformed completely to anatase TiO_2, as a consequence the BET surface area decreased to 60–70 m^2/g. It is interesting that even after phase

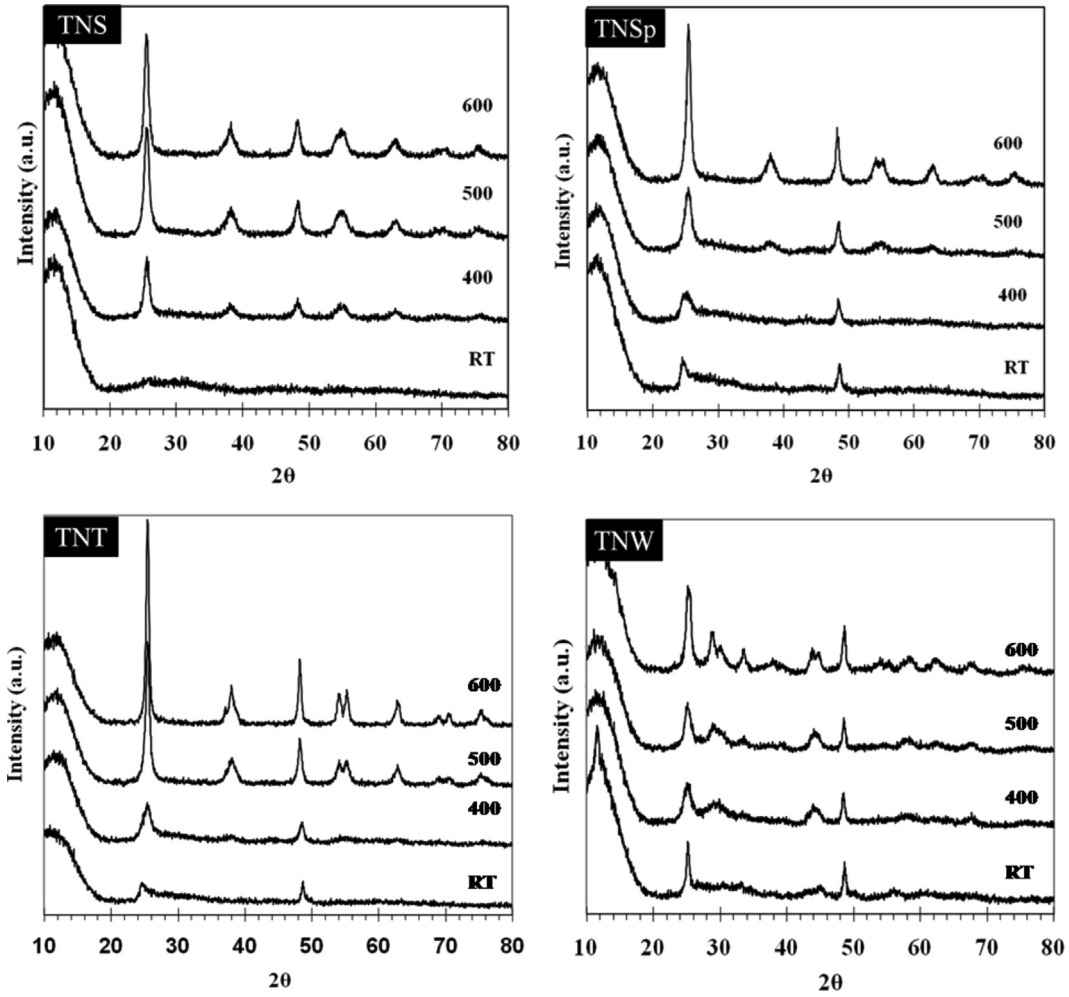


Fig. 4. XRD patterns of the nanostructure titanate after annealing at 400–600 °C.

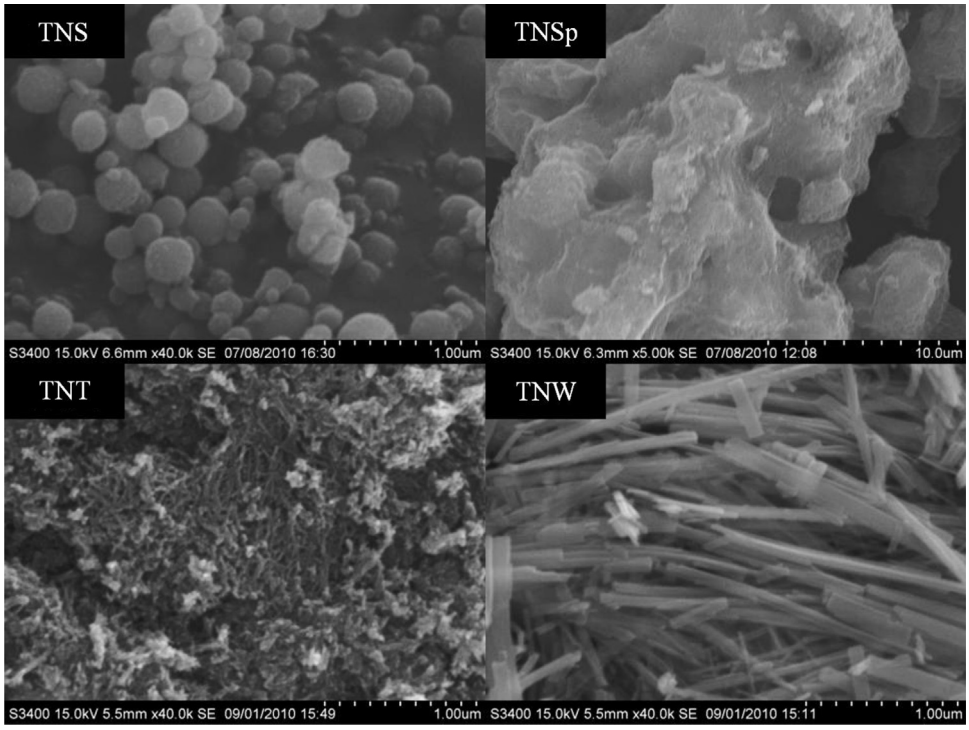


Fig. 5. SEM micrographs of the nanostructure titanate after annealing at 600 °C.

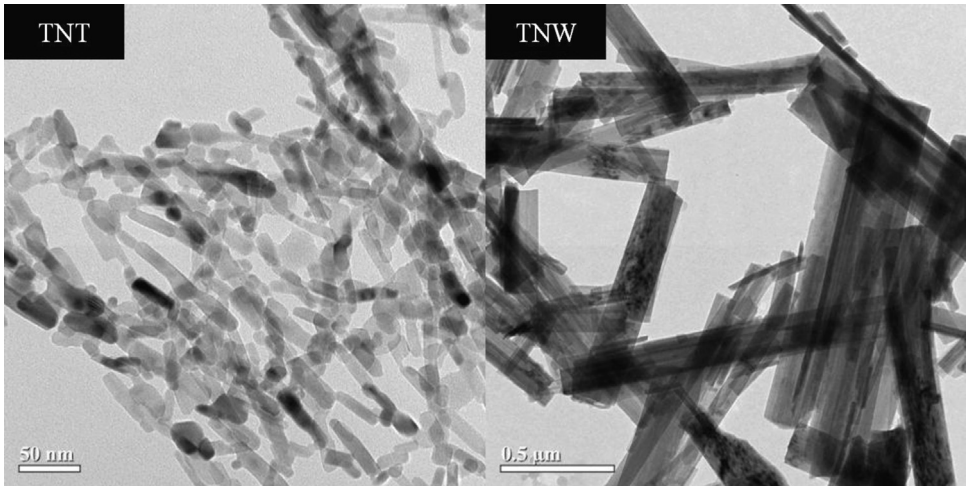


Fig. 6. TEM micrographs of the TNT and TNW after annealing at 600 °C.

Table 1
BET surface area of nanostructure titanate before and after annealing at 600 °C.

Sample	BET surface area (m^2/g)
TiO_2 commercial	4.8
Teflon vessel	
Spherical titanate (TNS)	211.1
TNS annealed 600 °C	71.7
Sponge titanate (TNSp)	211.9
TNSp annealed 600 °C	63.5
Teflon-lined autoclave	
Nanotube titanate (TNT)	192.0
TNT annealed 600 °C	63.0
Nanorod titanate (TNW)	23.2
TNW annealed 600 °C	19.4

transformation to anatase TiO_2, the annealed samples still possessed very high BET surface area comparing to the starting Com–TiO_2. However, phase transformation to anatase did not occur in the case of TNW and the BET surface area of annealed TNW sample was slightly changed.

4. Conclusions

Four different morphologies of the nanostructure titanate (sphere (TNS), sponge (TNSp), tube (TNT) and wire (TNW)) were successfully synthesized by using hydrothermal reaction of a spherical shape anatase TiO_2. The TNS and TNSp products with very high surface area (211 m^2/g) were formed under atmospheric pressure at 150 and 200 °C, respectively. While the TNT and TNW products were synthesized at 150 and 200 °C under autogeneous pressure, respectively. The formation of TNT and TNW was started from the dissolution of raw TiO_2 in NaOH solution accompanied by epitaxial growth of layered nanosheets of sodium titanates followed by the rolling up of the exfoliated titanate sheets to form nanotube or nanorod samples. However, without autogeneous pressure, the mechanism was different. It would start from the reaction between anatase TiO_2 and NaOH solution where small spherical particles of the titanates were formed and aggregated to form larger particles with an equivalent size of the raw TiO_2. When the reaction temperature increased the sponge particles were formed instead. After annealing at 600 °C, TNS, TNSp and TNT transformed back into anatase TiO_2 whereas annealing of the titanate nanowires resulted in metastable form TiO_2 under similar conditions.

Acknowledgments

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