

## 钛酸钠一维纳米结构的构筑

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**摘要:** 以锐钛矿  $\text{TiO}_2$  为起始原料, 通过水热法制备了钛酸盐纳米棒, 对合成不同长度和宽度的钛酸盐纳米棒的影响和控制条件进行了研究。用 X 射线衍射(XRD)和扫描电子显微镜(SEM)对纳米棒的形貌和结构进行了表征。结果表明水热温度和处理时间能对纳米棒的形貌和结构进行有效的控制, 得到理想的钛酸盐的结构。在更高的温度下(200  $^{\circ}\text{C}$ ), 钛酸盐纳米管将更快的转化为纳米棒, 而随着处理时间的延长, 其形貌结构发生有规律的变化。在 96 h 处理时间后纳米棒束的宽度为 50 nm 到 1  $\mu\text{m}$ , 长度可以达到几十微米。对后处理中酸洗对产物的形貌和晶体结构的影响也进行了对比研究, 发现在酸洗之前钛酸盐纳米棒结构就已经形成, 但是酸洗能使产物的晶体结构产生变化, 同时使纳米棒的表面形貌更加光滑规整。最后对比研究原料和产物的紫外-可见吸收光谱, 发现纳米管/棒在 250 至 350 nm 处有宽带隙吸收。

**关键词:** 钛酸盐; 水热法; 合成控制; 酸洗

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## Construction of One Dimensional Sodium Titanate Nanostructure

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**Abstract:** Titanate nanotubes and nanoribbons were synthesized hydrothermally, using anatase  $\text{TiO}_2$  as the starting material. The dependence of titanate nanoribbons length and width on control conditions was studied. The phase structure and the morphology were characterized by XRD and SEM. The results show that the morphology and the structure of titanate nanoribbons are controllable via changing the hydrothermal temperature and treatment duration of the titanate products. At higher temperature of 200  $^{\circ}\text{C}$ , titanate nanotube are transformed faster to nanoribbons and the morphologies are changed as a function of treatment duration. After the treatment duration goes up to 96 h, bundles of titanate nanoribbons are formed with widths ranging from 50 nm to 1  $\mu\text{m}$  and lengths up to tens of micrometers. Control experiments results show that the nanoribbons are formed before acid wash, but the morphology is more smooth and ordered after wash, and the crystal structure is changed during the acid wash process.

**Key words:** titanate nanoribbon; hydrothermal; synthesis control; acid wash

Nanomaterials and nanostructures have been the most energetic components in new material research over the past few years because of their potential applications. It has been aroused great interests since the carbon nanotube was found<sup>[1]</sup>. One-dimensional nanostructured materials including nanotubes, nanobelts,

nanorods and nanowires have attracted considerable attention due to their unique electronic and optical properties and their potential applications in modern technology<sup>[2]</sup>.

Recently, many approaches have been developed for the synthesis of nanomaterials based on metal ox-

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ides, such as  $\text{SnO}_2$ ,  $\text{VO}_2$ ,  $\text{ZnO}$ ,  $\text{Fe}_3\text{O}_4$ , and  $\text{TiO}_2$ <sup>[3]</sup>. The properties of these nonomaterials have been found to be dependent on their size and microstructure, so a good understanding of the synthesis mechanism and the effect on the size and shape of synthesis conditions such as reaction time or temperature, additives and post-treatment will be beneficial for more suitable applications<sup>[4-11]</sup>.

Among the nanomaterials and nanostructures,  $\text{TiO}_2$  is considered to be the most important one due to its unique physical and chemical properties.  $\text{TiO}_2$  is a broad band semiconductor and is chemically stable as well as stable toward photo-oxidation<sup>[12]</sup>. In addition, it is non-toxic and easily available and cheap.

One dimensional  $\text{TiO}_2$  nanostructure has been synthesized by various techniques at high- or low-temperature such as chemical vapor deposition, thermal evaporation, and hydrothermal method<sup>[13-15]</sup>. Since the first hydrothermal route reported by Kasuga et al<sup>[16]</sup>, it has been aroused great interest in the fabrication of nanotubes and nanoribbons. Yuan and co-workers<sup>[17]</sup> found that nanotubes could be formed at different temperatures (130~180 °C) and Elssah<sup>[3]</sup> reported that at given temperature, nanotubes could always transform into nanoribbons provided that the reaction time was long enough.

But most of these studies were just concentrated on the synthesis mechanism at low temperature (below 180 °C), or variation of the starting material, for example, using different crystal phases of  $\text{TiO}_2$  and different concentrations of  $\text{NaOH}$ <sup>[18]</sup>, few were involved in higher temperature and post-treatment studies. We report here the hydrothermal treatment at higher temperature of 200 °C and the control mechanism for the size and shape of the resulting products.

## 1 Experimental

### 1.1 Sample preparation

All the chemicals were analytical grade and used without further purification. 1 g of  $\text{TiO}_2$  nanopowder (average size: 32 nm) was added to 100 mL of 10 mol·L<sup>-1</sup>  $\text{NaOH}$  and stirred for 30 min in a beaker. The mixture was then transferred into different 100 mL Teflon-lined

stainless steel autoclaves up to about 80% of the capacity. The autoclave was put in the oven held at 200 °C for different treatment durations ranging from 6 to 96 h and then allowed to cool to room temperature. White floccule precipitate was collected and washed with distilled water until the pH value of about 7. Then the product was divided into two parts: one part was washed with 1 mol·L<sup>-1</sup>  $\text{HCl}$  and deionized water several times until the pH value of about 7 again, the other part was washed without acid solution. Both parts were then dried in air at 80 °C for 24 h.

### 1.2 Characterization

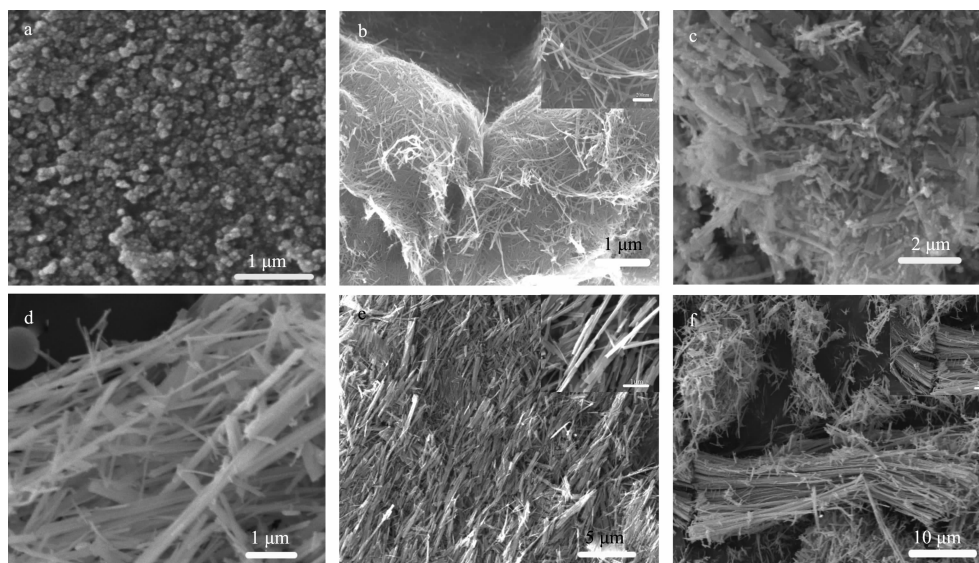
The samples were characterized by scanning electron microscopy (SEM, Philips FEI-XL30) operating at 25 kV and by X-ray powder diffraction (XRD, Analytical XpertPRO diffractometer with  $\text{Cu } K\alpha$  radiation,  $\lambda = 0.15418$  nm, 40 kV, 40 mA). The EDS analysis was performed through analytical scanning electron microscopy S-550. The UV-Visible spectra were obtained using a UV-Vis spectrophotometer (Hitachi UV-2000).

### 1.3 UV Spectroscopy

UV-Vis spectra were recorded at 25 °C for 100 mg·L<sup>-1</sup> titanate and anatase  $\text{TiO}_2$  well dispersed in quartz cells with a 10-mm path length, using distilled water as a blank.

## 2 Results and discussion

Fig.1 shows the SEM images of the commercial nanopowder samples used as the starting material and samples treated at 200 °C for different hydrothermal durations.  $\text{TiO}_2$  particles have a size ranging from 50 to 100 nm (Fig.1a). At relatively short treatment duration of 6 h, SEM results show that dense nanotubes are formed with diameters of about 10 nm and lengths up to several hundreds of nanometers.  $\text{TiO}_2$  crystal phase is changed, anatase phase is broken and expanded to anomalistic sandwich substance (Fig.1b). By increasing the treatment duration to 12 h, a few nanoribbons with different sizes are formed on the surface of anomalistic sandwich substance. The nanoribbons have width ranging from 50 to 500 nm and length of about 1 micrometer (Fig.1c). Increasing the treatment duration to 24 h, the anomalistic sandwich substance disappears, and inte-



(a) Anatase  $\text{TiO}_2$ ; (b) 6 h; (c) 12 h; (d) 24 h; (e) 48 h; (f) 96 h

Fig.1 SEM images of the anatase  $\text{TiO}_2$  and titanate nanoribbons synthesized by hydrothermally method at  $200^\circ\text{C}$  for different durations

grated dense nanoribbons are formed. The width also varies from 50 to 500 nm, and the length grows up to several micrometers (Fig.1d). At relatively long treatment duration (48 h), the nanoribbons keep growing, with average length up to 5  $\mu\text{m}$  (Fig.1e). After a very long treatment duration of 96 h, bundles of very long and wide nanoribbons are observed, the ribbons have length of several tens of micrometers and width variation between 50 nm and 1  $\mu\text{m}$  (Fig.1f).

It is obvious from these results that the hydrothermal treatment duration has a strong effect on the morphological features of the resulting products. We can see that under the strong alkali media, the materials morphology transforms gradually from spherical  $\text{TiO}_2$  particles to layer, then nanotube and lastly to nanoribbon bundles. A prevalent viewpoint about the mechanism of the formation of one dimensional titanate microstructure is that under the hydrothermal process of high temperature, high pressure and high alkali, Ti-O bonds of  $\text{TiO}_2$  particles are broken and expanded to layer structure. This layer structure has many unsaturated

bonds, resulting in high surface energy. As the hydrothermal duration extended, the layer structure would curl up to form nanotube, thus reducing the energy of the entire system. At the process of nanotube transformation into nanoribbon, this phenomenon can be explained by Ostwald Ripening<sup>[3]</sup>, i.e. many small crystals formed initially slowly disappear, except for a few that grow larger, at the expense of the small crystals, where the smaller crystals act as fuel for the growth of bigger crystals. If this process continues, eventually fewer and larger crystals form inside the solid that have much smaller surface-to-volume ratios compared to the smaller particles, thus reducing the energy of the entire system. This mechanism can explain the transformation to nanoribbons and to very long and wide bundles of nanoribbons with time. In consideration with other work on nanoribbons at lower temperature, we suggest that temperature takes effect on the synthesis rate on the formation of nanoribbons, but it is not the major factor for the morphology of the ultimate product. The model of hydrothermal synthesis process is shown in Fig.2.

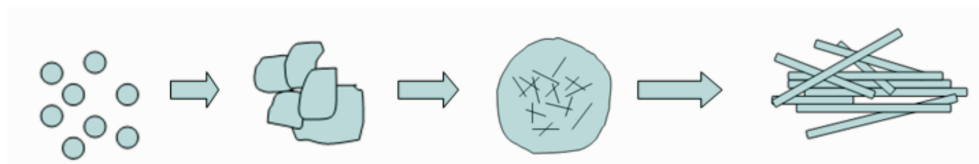
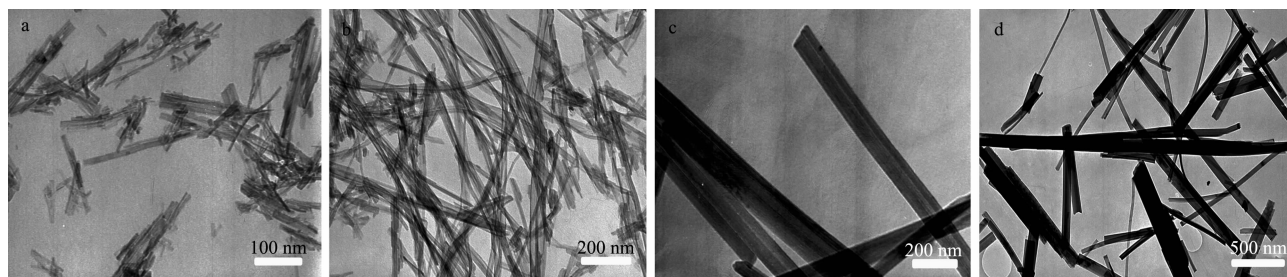


Fig.2 Simple model of hydrothermal synthesis process

Fig.3a shows the TEM micrograph of the sample treated at 200 °C for 6 h. The products are fine hollow open-ended tubes with a uniform diameter along their lengths. The titanate nanotubes are short and thin. Fig. 3b shows the nanotube produced in 12 h, the nanotube



(a) 6 h; (b) 12 h; (c) 24 h; (d) 48 h

Fig.3 TEM micrographs of the nanotubes and nanoribbons synthesized hydrothermally at 200 °C for different durations

A diagram of critical duration that titanate nanotubes transform into nanoribbons and the corresponding length of the titanate is plotted in Fig.4. The diagram describes the critical treatment duration needed for the titanate nanotube structure to transform into nanoribbon structure at 200 °C.

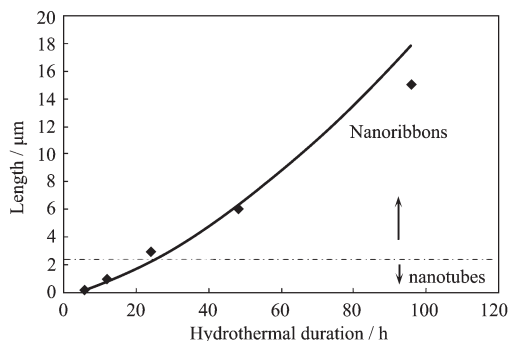
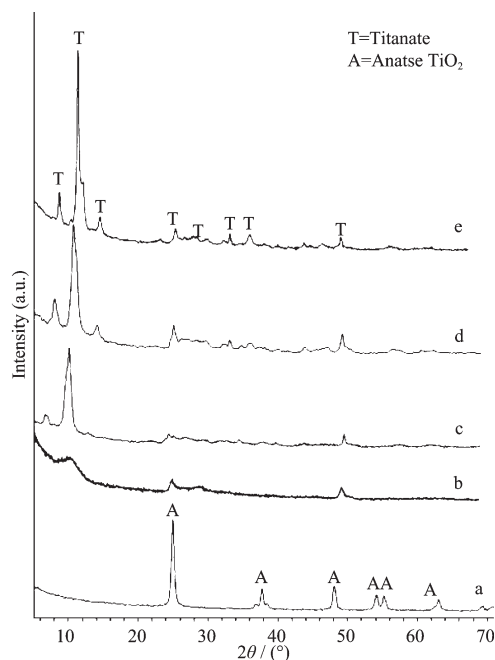


Fig.4 Diagram of the critical treatment duration needed for the transformation of nanotubes into nanoribbons and the corresponding length at 200 °C

Fig.5 shows the XRD patterns obtained. Fig.5a shows the crystal phase of starting material  $\text{TiO}_2$ , which can be assigned to the anatase crystal. From the XRD patterns, titanate crystals diffraction peaks are found at short treatment duration of about 6 h at 200 °C (Fig.5b), and accordingly  $\text{TiO}_2$  crystal phase is decreased or disappeared. As the treatment duration increases, the characteristic peaks for titanate are higher and sharper indicating the improved crystallinity (Fig.5c, Fig.5d and Fig.5e). After 96 h, the crystal is formed completely, which is composed of mixture H-titanate crystal phases

is longer and wider. For 24 h hydrothermal duration (see Fig.3c) some nanotubes were transformed into nanoribbons, bundles of very long and wide titanate are observed (Fig.3d). We can see that all of the products are nanoribbons.



(a) Anatase  $\text{TiO}_2$ ; (b) 6; (c) 24; (d) 48; (e) 96 h

Fig.5 XRD patterns of anatase  $\text{TiO}_2$  and products synthesized at 200 °C for different durations

mainly, mostly crystal phase is  $\text{H}_2\text{Ti}_3\text{O}_7$  ( $a=1.602$  nm,  $b=0.375$  nm,  $c=0.919$  nm; PDF card No.47-0561).

From the SEM and TEM results we can conclude that specific structure of titanate can be formed at given reaction temperature and duration under hydrothermal condition. The following table shows the relationship between treatment duration and morphology at 200 °C.

The SEM images and EDS analysis of the products are shown in Fig.6 with and without acid wash parts un-

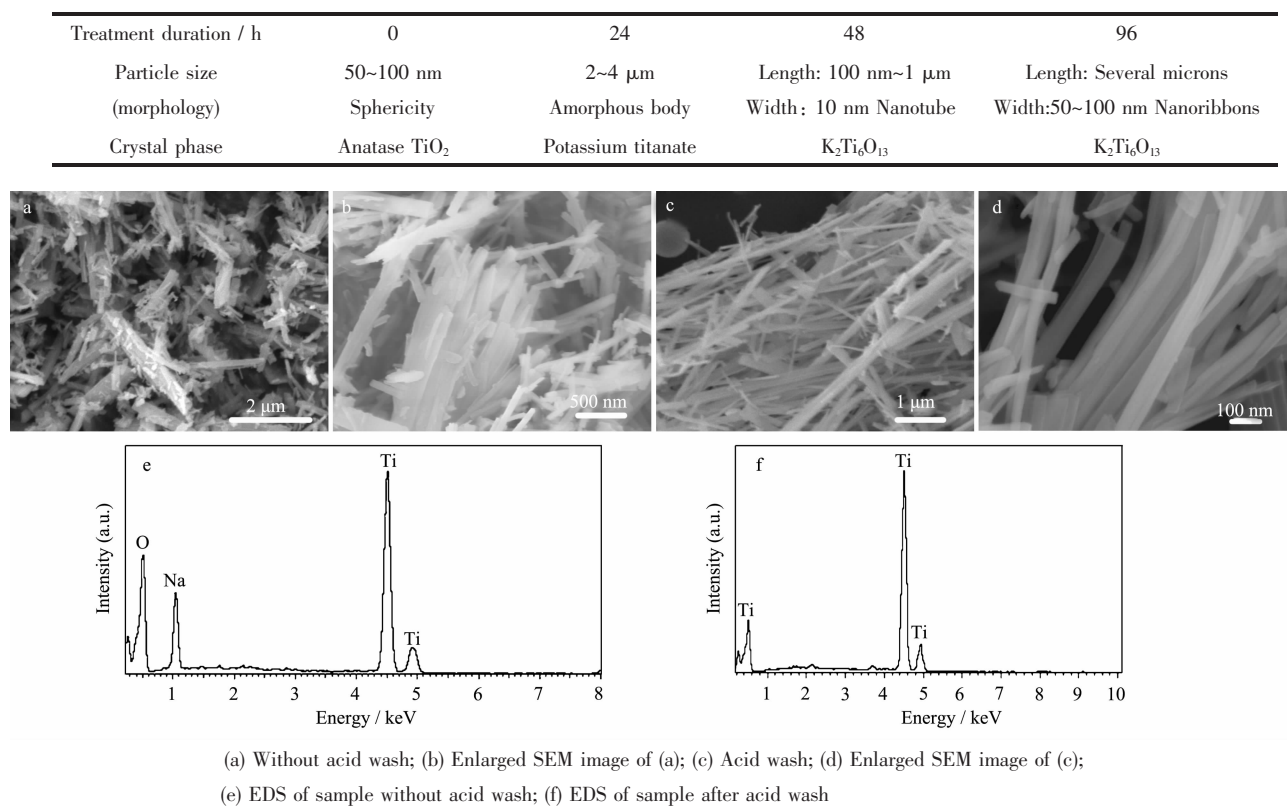


Fig.6 SEM images and EDS analysis of with and without acid wash in 24 h treatment duration at temperature of 200  $^{\circ}\text{C}$

der treatment temperature of 200  $^{\circ}\text{C}$  and treatment duration of 48 h. Fig.6a and its magnified image (Fig.6b) show that nanoribbons have been formed already at hydrothermal treatment process, this is different from the literature report. Nanoribbons are formed at acid wash process. The sample without acid wash is not much different from the acid wash part (Fig.6c and magnified image Fig.6d), whereas the nanoribbons without acid wash part also have width ranging from 50 to 500 nm and length of several micrometer. But the nanoribbons with acid wash part have more uniform crystal morphology. The EDS data (Fig.6e and Fig.6f) clearly indicate that the titanate nanotubes without acid wash part are composed of Na, Ti and O, as expected. There is no Na detected in the nanostructures, after washing with HCl.

The crystal phase of without acid wash part was a mixture of sodium titanates as in Fig.7. Most of the relatively sharp peaks of acid wash part belong to the hydrogen titanate due to the washing process with HCl, where the residual  $\text{Na}^+$  ions are replaced by  $\text{H}^+$  ions. The crystal phase also changes during the acid wash process. We can see from these results that crystal

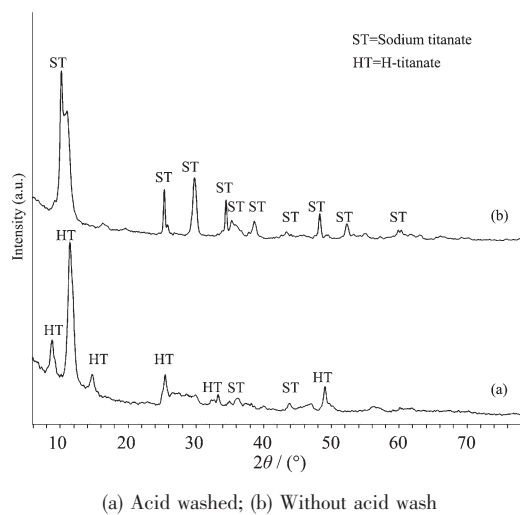


Fig.7 XRD patterns of titanate products in 48 h treatment duration at temperature of 200  $^{\circ}\text{C}$

phase results in the change of the modality.

Fig.8 shows the UV-Vis absorption spectra of anatase  $\text{TiO}_2$  and titanate nanoribbons with 24 h and 48 h hydrothermal treatment duration. From this Figure it is obvious that for all the samples there is a broad band absorption from 250 to 350 nm, due to the transition from the  $\text{O}^{2-}$  antibonding orbital to the lowest empty or-

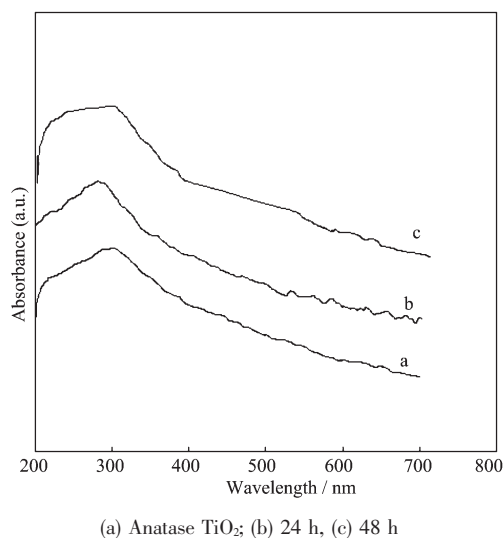


Fig.8 UV-Vis spectra of anatase TiO<sub>2</sub> and titanate products of 24 h and 48 h treatment durations

bital of Ti<sup>4+</sup>[19]. It is clear that the absorption properties alter significantly. A blue shift is found for the titanate products with treatment duration of 24 h compared with that of 48 h. This blue shift can be rationalized that with decreasing in sample size, the optical edge tends to shift to higher energy, a phenomenon attributed to quantum size and confinement effects<sup>[20]</sup>. The positions of the absorption peaks of anatase TiO<sub>2</sub> and titanate nanoribbons suggest that these materials are wide band gap semiconductors.

### 3 Conclusions

In summary, at temperature of 200 °C, shorter time is needed to form nanoribbons, indicating that the higher the temperature, the faster the integrated nanoribbons, but temperature has no much effect on the final morphology of titanate as far as the temperature is high enough. As the treatment duration extended, the morphological structure of the synthesized product change a lot. Our results show that longer time may lead to longer and more uniform nanoribbons. It is found that nanoribbons have been already formed in hydrothermal process, but the acid wash step is beneficial for more

smooth and ordered morphology of the products. It is also possible that the results may look different if the starting nanopowder is changed; therefore further study on the effect of different starting nanopowders is needed.

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