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## Influence Of Calcination Temperatures On The Structure Of Nanocrystalline Mesoporous Titania



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### ABSTRACT

Well-organized mesoporous titania with nanocrystalline anatase framework was successfully synthesized by using tetrabutyl titanate as the inorganic precursor and triblock copolymer (Pluronic P123) as the template via sol-gel method. The resulting materials were characterized by thermogravimetric analysis (TGA), small-angle XRD, wide-angle XRD, high resolution transmission electron microscopy (HRTEM) and scanning electron microscopy (SEM). Calcination temperatures plays a pivotal role in both the framework and the mesostructure of mesoporous titania. We also proposed that well-ordered mesoporous titania will be gained by reasonably dominating processes of removal of the template and crystallization.

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### KEYWORDS

Mesoporous titania;  
Anatase;  
Nanocrystalline;  
Calcination Temperatures;  
Structure.

### INTRODUCTION

Since Antonelli and Ying reported a modified sol-gel synthesis of hexagonally packed mesoporous titania<sup>[1]</sup>, mesoporous titania has attracted much attention because of its great significance in solar cell

electrodes<sup>[2-4]</sup>, photocatalysis<sup>[5-6]</sup>, gas-sensors<sup>[7]</sup>, electrochromic display devices<sup>[8]</sup> and other applications<sup>[9-10]</sup>. Therefore, mesoporous titania materials have been extensively studied in recent years.

However, it's very difficult to synthesize well-ordered mesoporous titania due to the high reactiv-

ity of titania precursors toward hydrolysis and condensation and the instability of the inorganic framework upon removal of the template. In principle, mesostructure may be destroyed through elimination of the template by either calcination or extraction. For instance, removal of the template by extracting procedures can lead to complete dissolution of the material due to an insufficiently condensed inorganic framework. Calcination of materials is also not desirable, resulting in poorly ordered materials or dense fully collapsed structures<sup>[11]</sup>. Hence it is of great significance to study the influence of calcination temperatures on the structure of mesoporous titania.

In the work reported in this article, mesoporous titania samples were successfully synthesized via sol-gel method and calcination was used to remove the template. Calcination temperature plays a pivotal role in successful synthesis of mesoporous materials<sup>[11-12]</sup>. However, there are few reports about influence of calcination temperatures on the structure of mesoporous titania, to our best knowledge. Here, we have conducted intensive researches on this program.

## EXPERIMENTAL

### Preparation of samples

Mesoporous titania materials were prepared according to the following method. The pluronic P123 was kindly donated by BASF. 4.3 g P123 was first dissolved in 50 ml ethanol, then 0.6 ml 1 M hydrochloric acid solution was added to above solution under vigorous stirring for 3 h. Separately, 10.2 ml tetrabutyl titanate (abbreviated as TBOT) and 1.5 ml acetylacetone (abbreviated as AcAc) were mixed by stirring about 0.5 h, and then added to P123 and ethanol solution. After 0.5 h, 16 ml distilled water was added to the mixed solution, subsequently aged with vigorous stirring at room temperature for about 6 h. The fresh transparent reactant solution was poured in a beaker and aged at 40°C until it became gelatin. As-synthesized gelatin was subsequently calcined at different temperatures.

### Characterization of materials

Thermogravimetric analysis was obtained on 409 PG/PC different scanning calorimeter. The power

X-ray diffraction patterns were obtained by a Rigaku D/max 2550 diffraction using a high power Cu K $\alpha$  source operating at 40 kV and 200 mA. HRTEM images were obtained on using Hitachi-H800 microscopy operating at an acceleration voltage of 200 kV.

## RESULTS AND DISCUSSION

### Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out to determine optimal calcination temperature from room temperature to 500°C. Figure 1 shows TG-DSC trace of dried gelatin of mesoporous titania. Below 120°C, mass loss is due to volatile species, such as water, ethanol, butanol, and HCl. Between 120°C and 330°C, comparative large mass loss arises from the decomposition of the P123 template. Based on this TGA trace, the template will be completely removed after 330°C.

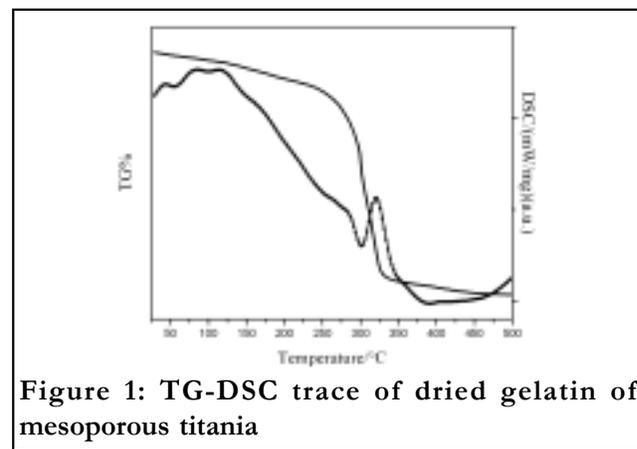


Figure 1: TG-DSC trace of dried gelatin of mesoporous titania

### Influence of calcination temperatures on mesoporous titania

Typically, elimination of the template by calcination is widely used to obtain mesostructure. However, optimizing the calcination temperature is a prerequisite for well-organized mesoporous materials. On one hand, the template can't be completely removed at low temperature; on the other hand, high temperature will result in either poorly ordered materials or dense fully collapsed structures<sup>[11,13-14]</sup>. Influence of calcination temperatures on the structure of mesopores and framework was discussed by XRD results. Figure 2 represented the small-angle XRD patterns of as-synthesized samples after calcined at

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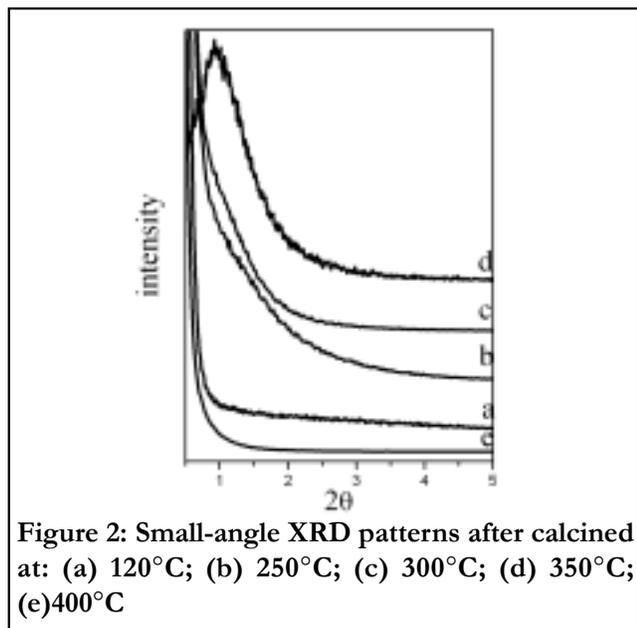


Figure 2: Small-angle XRD patterns after calcined at: (a) 120°C; (b) 250°C; (c) 300°C; (d) 350°C; (e) 400°C

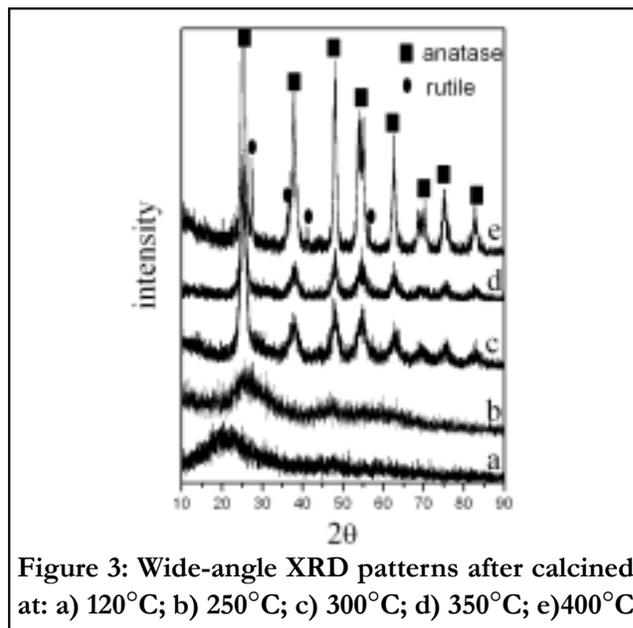


Figure 3: Wide-angle XRD patterns after calcined at: (a) 120°C; (b) 250°C; (c) 300°C; (d) 350°C; (e) 400°C

120°C (curve a), 250°C (curve b), 300°C (curve c), 350°C (curve d) and 400°C (curve e) separately, and corresponding wide-angle XRD patterns were shown in figure 3. No diffraction peaks appeared in small angle after calcined at 120°C, which indicated that mesostructure was not formed or poorly ordered. And the obtained material was amorphous titania. Amorphous titania began to crystallize to anatase as calcination temperature raised to 250°C, from characteristic diffractions peaks of anatase (Figure 3b). Although most part of the sample turned to anatase after calcined at 300°C (Figure 3c), no diffraction peaks appeared in the small angle (Figure 2c). When temperature up to 350°C, well-organized mesoporous titania with framework of nanocrystalline anatase was obtained according to figure 2d and figure 3d. Rutile phase was appeared (Figure 3e) but small angle diffraction peak was disappeared (Figure 2e) after calcined at 400°C, which would prove that mesopores were collapsed and destroyed at high temperature.

It can be seen from above discussion that well-organized mesoporous titania could be formed with framework of anatase phase. Uncompletely crystallization of amorphous titania and appearance of rutile phase will lead to poor order of materials. The porosity of anatase phase interparticles consists of mesopores, which is consistent with previous reports<sup>[15]</sup>. The size and morphologies of mesopores are roughly determined from the size and morpholo-

gies of hydrophobic core of the template<sup>[11]</sup>. With the removal of template, amorphous titania began to crystallize, which may comprise following steps: (1) interface nucleation of anatase on contact areas of amorphous particles; (2) crystal growth of anatase by redistribution of atoms from either amorphous particles or smaller anatase crystals onto nanocrystal surfaces; (3) oriented attachment of adjacent anatase particles that are in appropriate orientations<sup>[16]</sup>. Interface nucleation, crystal growth and oriented attachment upon calcination, must cause volume variations, defects formation, and crystal excessive growth and so on. And all these will destroy thin framework, or deteriorate the size and shape of pores which formed by the template previously, lead to poorly ordered mesostructure or fully collapsed structures. It may be the main reason why obtaining well-ordered mesoporous titania is so difficult. If we can obtain anatase network before removal of template, reduce the influence of phase transition, and control the appropriate crystallization rate, well-ordered mesoporous titania with crystalline wall can be prepared.

#### Characterization of well-organized mesoporous titania

Figure 4 shows small-angle XRD and wide-angle XRD patterns of mesoporous titania after calcined at 350°C. The small-angle XRD pattern showed a very sharp peak in  $2\theta = 0.92^\circ$ , which demonstrated

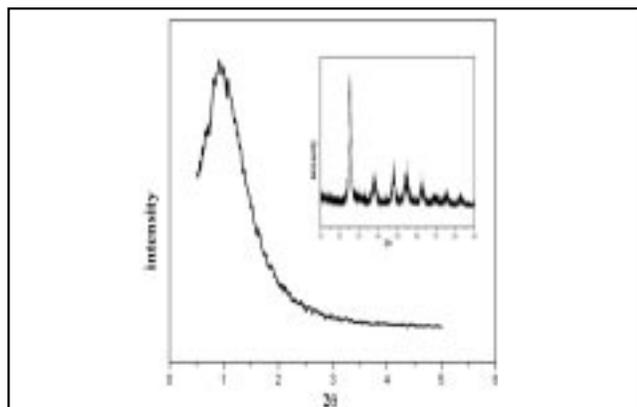


Figure 4: Small-angle XRD and wide-angle XRD (inset) patterns of mesoporous titania after calcinations

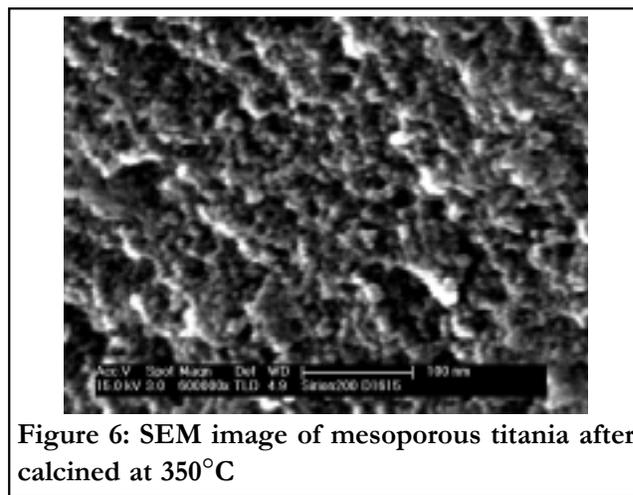


Figure 6: SEM image of mesoporous titania after calcined at 350°C

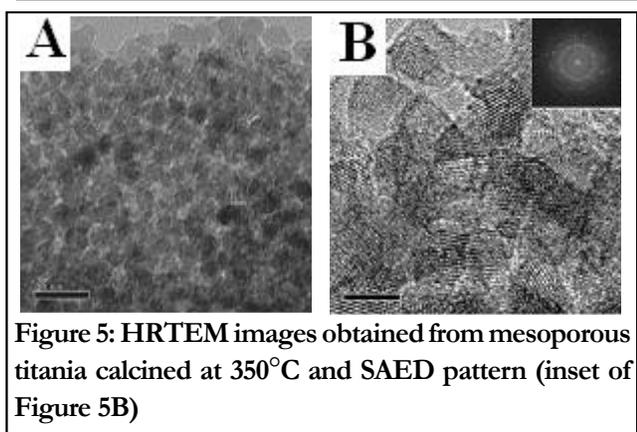


Figure 5: HRTEM images obtained from mesoporous titania calcined at 350°C and SAED pattern (inset of Figure 5B)

that well-organized mesostructure had been formed. The wide-angle XRD pattern clearly represented the presence of nanocrystalline anatase, which has been further confirmed by HRTEM results (SAED pattern inset of figure 5B). As calculated from Scherrer equation using the (101) diffraction peak, the average crystallite size was about 8.5 nm.

HRTEM images of calcined samples shown in figure 5A verified a thermally stable and well-organized mesostructure. Its average pore size estimated from HRTEM was about 5 nm. From the HRTEM images (Figure 5B), it reveals that framework of mesoporous titania calcined at 350°C was consisted of anatase nanocrystallites. D-space was found to be about 3.4 Å, which was well consistent with the results of wide-angle XRD. SEM image shows morphologies of mesoporous titania. The mesopores were formed by packed nanocrystalline.

## CONCLUSIONS

This work shows that well-organized mesoporous titania with nanocrystalline framework consisting of a titania anatase phase was successfully synthesized by using TBOT as the inorganic precursor and triblock copolymer P123 as the template. Calcination temperatures have a strong impact not only on the framework but also on the formation of mesostructure. Well-ordered mesoporous titania will be gained by reasonably dominating processes of removal of the template and crystallization from amorphous titania into anatase upon calcination. Further study is in progress.

## ACKNOWLEDGEMENTS

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