

## Low Temperature Synthesis of Titanium Oxide

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A new solution-based synthesis technique has been developed to synthesize crystalline rutile-type  $\text{TiO}_2$  particles at a low temperature. Layered perovskite titanates,  $\text{NaLnTiO}_4$ , ( $\text{Ln}$  = rare earth) with an ordered  $\text{K}_2\text{NiF}_4$  type structure were dissolved into  $\text{HNO}_3$  solution to give crystalline rutile titania at 90 °C. A crystalline  $\text{TiO}_2$  powder was obtained by evaporation of the dissolved powder in  $\text{HNO}_3$  solution. As-prepared powders were characterized by powder X-ray diffraction (XRD), fluorescence X-ray analysis (XRF), and scanning electron microscopy (SEM).

Key words: Solution, Titanate, Titania, Layered perovskite, Rutile

### 1. INTRODUCTION

Crystalline titania ( $\text{TiO}_2$ , anatase and rutile) has attracted much attention because of its wide applications such as white pigment, photocatalyst, and electrode [1, 2]. The titania has three polymorphism; rutile, anatase and brookite. The rutile, a common form of the titania, is the most thermodynamically stable phase [3]. Therefore, the rutile is also the most suitable material for white pigments and coatings because of its high refractive index and chemical stability [4].

In industry, crystalline titania is produced from natural ilmenite or rutile ores as a starting material using either a sulfate or chloride process at high temperatures [4]. Although the chloride process will eventually become a preferred process, this process produces hazardous by-products such as  $\text{Cl}_2$  and  $\text{HCl}$ . Therefore, cost-saving and safety processes are required for the synthesis of the crystalline titania.

In this study, we report a new solution-based manufacturing process for the production of fine titania particles. A layered perovskite compound,  $\text{NaLaTiO}_4$ , with an ordered  $\text{K}_2\text{NiF}_4$  type structure was dissolved into an aqueous  $\text{HNO}_3$  solution to give crystalline rutile titania particles at 90 °C. The effect of the synthetic conditions on the crystallinity, microstructure and photocatalytic activity of the obtained crystalline  $\text{TiO}_2$  powders was investigated.

### 2. EXPERIMENTAL

Powder  $\text{NaLaTiO}_4$  samples were prepared by a conventional solid-state reaction. The starting materials were a mixture of sodium carbonate, lanthanum oxide,

titanium oxide. An excess amount of sodium carbonate (30 mol%) was added to compensate for the loss due to the evaporation of sodium component. The mixtures were heated for 10-30 min at 900-1000 °C. The layered titanate powder (0.1 g) were gradually dissolved in the 10 M  $\text{HNO}_3$  solution (10 ml) at room temperature. Transparent solution was stable for 1 week without any precipitation. After the evaporation (90 °C) of solution, the powder was washed with a distilled water and dried in oven at 50 °C. The phase of powder samples was confirmed by the powder XRD using a Mac Science MX-Labo diffractometer. The purity of sample was characterized by the XRF. Morphology of titania powder was observed using SEM. The Photocatalytic activity of the samples was evaluated by measuring decomposition rates of a methylene blue solution under an UV lamp irradiation. Band gap energy of titania sample was determined from the diffuse reflectance spectra of the powder.

### 3. RESULT AND DISCUSSION

The synthesis of the layered perovskite compounds,  $\text{NaLnTiO}_4$  ( $\text{Ln}$  = La, Nd, Sm, Gd, Dy, Y, Tm, and Lu), was first reported by Blasse [5]. He claimed from the indexing of the powder X-ray diffraction (XRD) patterns that the interlayer cations in layered titanate  $\text{NaLnTiO}_4$  are ordered between the two available interlayer sites. However, there has been no direct evidence that such ordering really exists in  $\text{NaLnTiO}_4$ . Until recently, the structure refinements of these compounds have not been carried out. As shown in Fig.1, we have reported the

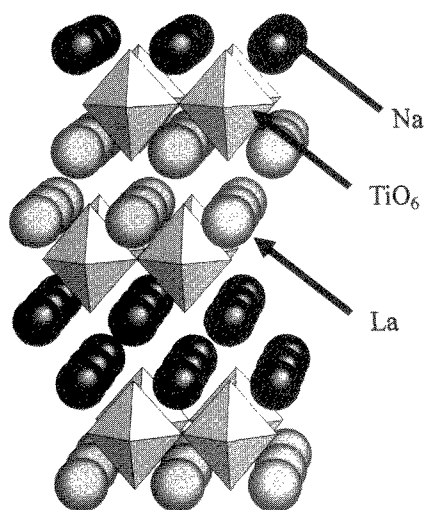


Fig.1 Crystal Structure of layered perovskite NaLaTiO<sub>4</sub>.

crystal structure of layered perovskite compounds, NaLnTiO<sub>4</sub> in recent paper [6, 7]. The dissolution behavior can be explained by weak interaction between the perovskite layer and the interlayer sodium ions in NaLaTiO<sub>4</sub>. The rare earth "LaO" layer in NaLaTiO<sub>4</sub> is positively charged and the sodium "NaO" layer is negatively charged. Since the perovskite layer is thought to be electrically neutral, the interaction between the perovskite layer and the interlayer cation is relatively

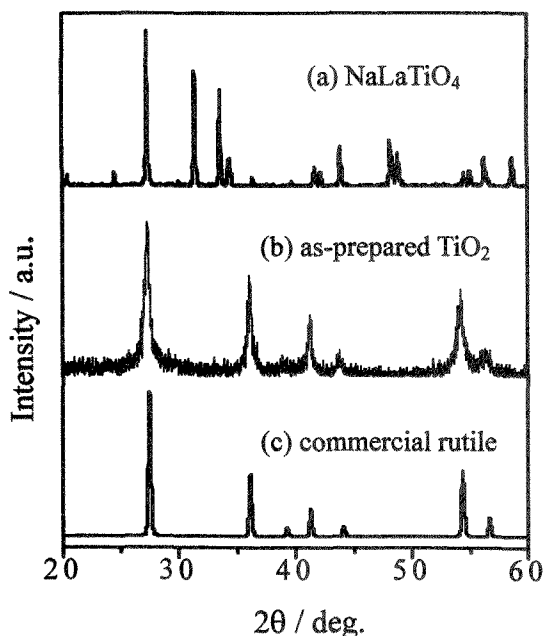


Fig. 2 Powder XRD patterns of (a) NaLaTiO<sub>4</sub>, (b) as-prepared TiO<sub>2</sub>, and (c) commercial rutile TiO<sub>2</sub>.

weak. Therefore, the incorporation of HNO<sub>3</sub> solution is possible for the interlayer of NaLaTiO<sub>4</sub>.

Fig. 2 shows the XRD patterns of (a) precursor NaLaTiO<sub>4</sub> and (b) precipitates after evaporation. The XRF data indicated that there is no detectable amount of sodium and lanthanum component after the washing. Therefore, it was found that a single phase of the crystalline rutile was formed after evaporation at 90 °C. This process yields only the rutile crystal structure. On the other hand, the behavior of HCl solution contrasts markedly with that of HNO<sub>3</sub> solution. When the HCl solution was evaporated at 90 °C, crystallization of titania could not occur. This fact means the nitrate ion can act as a mineralizer in the formation of crystalline TiO<sub>2</sub>.

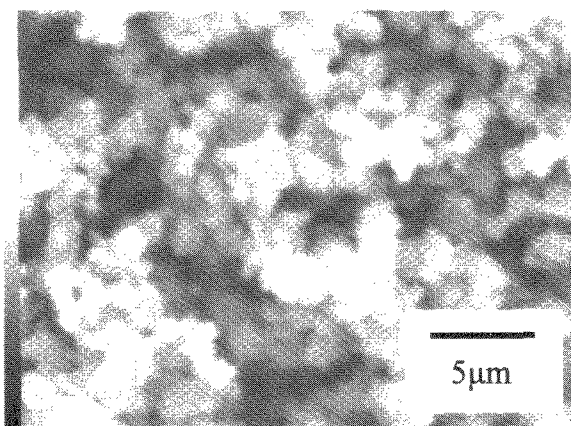


Fig. 3 SEM photograph of the rutile-type TiO<sub>2</sub> prepared by the evaporation at 90 °C.

Fig.3 showed the SEM photograph of the rutile TiO<sub>2</sub> prepared by the evaporation at 90 °C. The rutile powders were agglomerations of particles with the size of about 0.5 – 2 μm. Fig. 4 shows diffuse reflectance spectra of the powder sample. The band gap energy of the soft chemical TiO<sub>2</sub> is comparable to that of the commercial rutile titania. Therefore, soft chemical product can be used as the white pigments and coatings.

Fig. 5 showed the photocatalytic activities of the as-prepared TiO<sub>2</sub>, soft chemical TiO<sub>2</sub> annealed at 600 °C and commercial rutile powder. The soft chemical sample without the high temperature annealing does not have the photocatalytic activity for the decomposition of the organic pollutants. As shown in Fig. 6, the as-prepared TiO<sub>2</sub> reduces the weight for the heating. These results suggest that the as-prepared TiO<sub>2</sub> is thinly coated with the inactive amorphous component, indicating the importance of the crystallinity of the titania surface for photocatalytic activity. The rutile titania without photocatalytic activity is particularly appropriate for the white pigment. On the other hand, the situation requires

that the surface losses such as “dead layer” should be minimized in the photocatalytic application of soft chemical  $\text{TiO}_2$ .

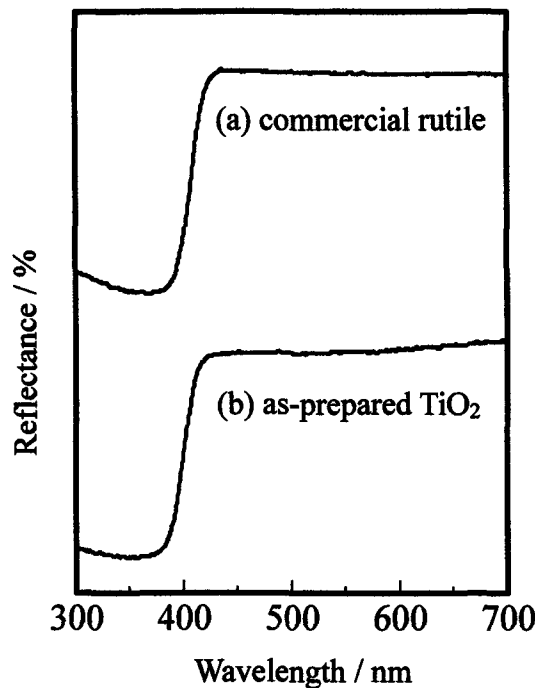


Fig. 4 The diffuse reflectance spectra of (a) commercial rutile and (b) as-prepared  $\text{TiO}_2$ .

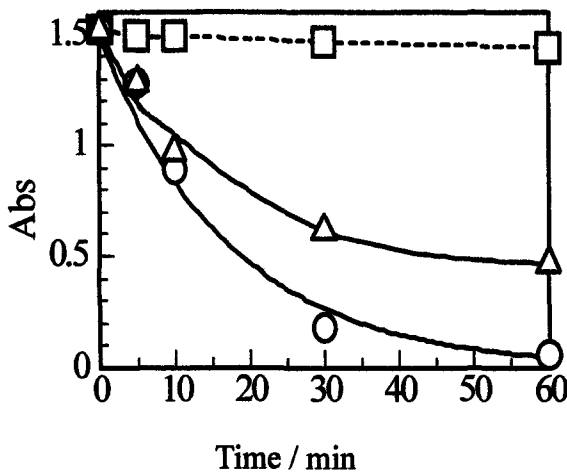


Fig. 5 Photocatalytic activities of (□) as-prepared  $\text{TiO}_2$ , (Δ) soft chemical  $\text{TiO}_2$  annealed at  $600^\circ\text{C}$  and (○) commercial rutile.

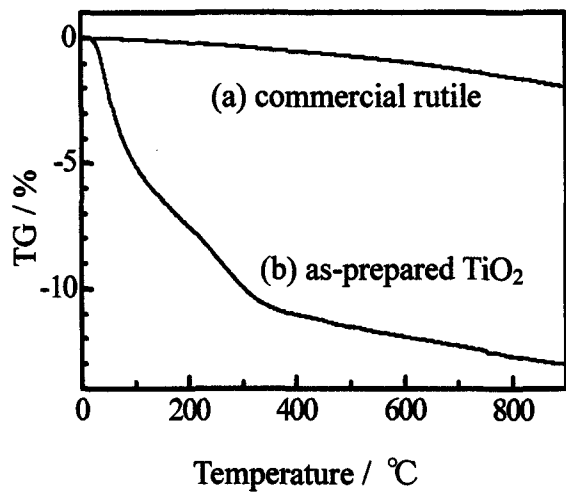


Fig. 6 TG curves of the (a) commercial rutile and (b) as-prepared  $\text{TiO}_2$ .

As shown Fig. 7, our preliminary work shows that the natural rutile ore (95 % $\text{TiO}_2$ ) could be used in preparing the high purity layered precursor,  $\text{NaLaTiO}_4$ . In addition, the sodium and lanthanum components were reproduced directly from the rinsed water of the titania powders. Therefore, this soft chemical route is a cost-saving and safety process for low-temperature synthesis of pure rutile titania. Characteristics of the new solution method is the elimination of the anion impurities such as chloride or sulfate. It is well-known that the anion ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , etc.) affects the phase and the morphology of the titania precipitate [8]. Detailed quantitative investigations to understand the impurity effect of anatase-rutile transformation are being performed.

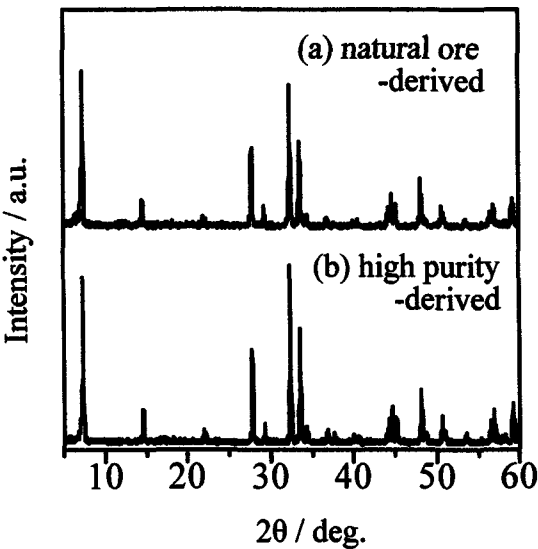


Fig. 7 Powder X-ray diffraction patterns of (a) natural rutile ore - derived and (b) high-purity raw material - derived  $\text{NaYTio}_4$ .

#### 4. CONCLUSION

A new soft chemical process was developed for synthesizing fine titania particles using the aqueous  $\text{HNO}_3$  solution as the reaction medium at 90 °C. The tailored solution may be advantageous for preparing of fine particles or fabrication of thin films. The developed soft chemistry process is a general and powerful tool for synthesizing the pure titania from natural rutile ore. To the best of our knowledge, no such a low temperature synthetic process of the pure titania has been found up to now.

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