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# Thermal stability of heat-treated flame-synthesized anatase $TiO_2$ nanoparticles

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**Abstract** In this article, $TiO_2$ nanoparticles were synthesized by using $O_2$-enriched coflow, hydrogen, diffusion flames. We investigated the thermal stability of the flame-synthesized $TiO_2$ nanoparticles by examining the crystalline structures of the nanoparticles and by analyzing the photocatalytic degradations of methylene blue solutions. Also, the results were compared with those of commercial P-25 nanoparticles. The maximum centerline temperature of the flame was measured to be 1,743 °C. Under this synthesis condition, $TiO_2$ nanoparticles, which were spherical with diameters approximately ranging from 30 to 60 nm, were synthesized. From the XRD analyses, about 96 wt.% of the synthesized nanoparticles were anatase-phase. After the heat-treatment at 800 °C for 30 min, the synthesized $TiO_2$ nanoparticles showed no significant changes of their shapes and crystalline phases. On the other hand, most of the commercial particles sintered with each other and changed to the rutile-phase. Whereas the photocatalytic ability of heat-treated commercial particles deteriorated, that of the flame-synthesized particles improved. On the basis of the improved result of photocatalytic degradation of methylene blue by using the heat-treated flame-synthesized nanoparticles, it is believed that the flame-synthesized $TiO_2$ nanoparticles have higher thermal stability at 800 °C than the commercial particles.

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## Introduction

Titania ($TiO_2$) nanoparticles are well known photocatalytic materials. They crystallize into mainly two polymorphic forms: anatase and rutile [1]. Anatase titania particles are chemically and optically more active in environmental remediation than rutile particles. Because of the photocatalytic properties of anatase particles, much research has been focused on the application of these particles in the treatment of organic dye in aqueous solution [2], and in the degradation of gas phase organic compounds by using the anatase particles as a support for metal-oxide [3] and the elemental mercury [4].

Anatase is a metastable phase, so the nanoparticles can be transformed into rutile at high-temperatures [1]. The onset temperatures for the transformation of prepared anatase particles into rutile particles using a heat-treatment range from 650 to 800 °C depending on the compact structure of the titania pellet [5] and the silica additive contents [6]. Xia et al. [7] also showed the same transformation of anatase particles into rutile particles by heat-treatment of titania nanoparticles prepared by vapor-phase hydrolysis.

In 1972, Formenti et al. [8] synthesized several metal oxide particles with diameters in the range of 10–200 nm by carrying vapor of metal chloride in the hydrogen-oxygen flame. Fotou et al. [9] reported the photodestruction of phenol in non-aerated aqueous solutions under UV-irradiation by using flame-synthesized titania powders. The destruction rates of their powders were comparable with or better than those of commercial powders. In 1995, the effect of dopants, such as $SiCl_4$, $SnCl_4$, $AlCl_3$, and $Al_2O_3$, on the characteristics of titania particles made by oxidation of $TiCl_4$ in a laminar diffusion flame reactor was investigated by Vemury and Pratsinis [10]. They showed that silica

decreases the sintering rate of titania and decreases the primary particle size, and as a result, the specific surface area increases.

To prepare the $TiO_2$ nanoparticles, Jang et al. [11] used the oxidation of $TiCl_4$ in a diffusion flame reactor. The effects of particle size and phase composition of these particles on the photocatalytic properties such as the decomposition of methylene blue, bacteria, and ammonia gas were investigated. Katzer et al. [12] also investigated the effects of a DC electric field on the growth processes of titania particles formed in a premixed $CH_4$–$O_2$ flame for several types of electrode geometries.

Yang et al. [13] utilized three different burners to obtain a wide range of flame processing conditions. Mixtures of anatase and rutile-phase titania nanoparticles were obtained at low reaction temperatures between 900 and 1,430 °C. Spherical particles of 100% anatase titania were obtained at high-temperatures between 1,500 and 1,570 °C. In our previous article [14], we reported the same tendency as that of Yang et al. [13] of the effect of flame temperature on the diffusion flame synthesis of anatase nanoparticles. Yeh et al. [15] also reported that the anatase content of titania particles created in flames was increased with the increase of the oxygen concentration in the oxidizer. The enhancement of the coalescence of nanoparticles by use of laser beam irradiation on aggregates formed in flames was reported by Lee and Choi [16]. They showed that stable rutile titania particles transformed into metastable anatase particles through the $CO_2$ laser irradiation.

Recently, researchers have carried out degradation of organic pollutants such as phenol, *p*-nitrophenol, and salicylic acid by using flame-synthesized $TiO_2$ nanoparticles [17]. They reported the solar photocatalytic degradation of various dyes such as methylene blue, remazol brill blue B and orange G. The results obtained by using flame-synthesized $TiO_2$ nanoparticles were compared with those of commercial Degussa P-25 $TiO_2$ nanoparticles for similar conditions [18]. Akurati et al. [19] also reported the photocatalytic decomposition of methylene blue. Their flame-synthesized $TiO_2$ particles showed improved photocatalytic activity compared to the commercial P-25 particles.

As shown in previous articles [5–7], the onset temperatures of the transformation of the prepared anatase particles into rutile particles ranged from 650 to 800 °C. To determine the phase transformation characteristics of the flame-synthesized $TiO_2$ nanoparticles, we produced and sintered the nanoparticles. The degradation of organic pollutants was measured to determine the photocatalytic activity of the heat-treated nanoparticles. In this article, we synthesized $TiO_2$ nanoparticles by using an $O_2$-enriched coflow hydrogen diffusion flame. We investigated the thermal stability of the flame-synthesized $TiO_2$ nanoparticles. The axial flame temperatures were measured to determine the representative temperatures for the flame condition. Also, SEM (scanning electron microscope) image analysis was used to examine the sizes and shapes of the sampled particles. The crystalline phases of the $TiO_2$ nanoparticles were also investigated by using X-ray diffraction (XRD). The photocatalytic degradation of organics with UV light irradiation was also analyzed.

## Experimental

The experimental setup consisted of several gas and mass flow controllers with readout units (Kofloc Co. Ltd.), a burner and a flame used as a hydrolysis reactor, a horizontal traverse with a controller for particle sampling and temperature measurement, and a two-dimensional traverse system for moving the burner. The burner used in this study consisted of three concentric tubes of 3.87, 16.57, and 70.0 mm inner diameters. The argon gas used as a carrier gas for the precursor was delivered through the central tube via the evaporator of the TTIP ($Ti[OCH(CH_3)_2]_4$, titanium tetraisopropoxide, Kanto Chemical Co., Inc., purity >97%) precursor. The precursor was used without any further purification. The evaporator was maintained at a temperature of 80 °C. The fuel, hydrogen, was supplied through the second tube. The oxygen was premixed with air, and then the mixture was passed through the outer tube, which was the third tube. The experimental conditions regarding the flowrates of the gases are provided in Table 1. The oxygen content in the oxidizer mixture, which was supplied through the outer tube, was supplied to elevate the flame temperature.

The synthesized nanoparticles were sampled on the thermophoretic plates placed at 230 mm H.A.B. (Height Above the Burner). A fine wire R-type thermocouple (Pt/Pt–13%Rd, diameter of the wire = 0.127 mm) was used to measure the centerline temperatures of the flame.

The crystalline phases of the collected $TiO_2$ nanoparticles from the plates and thermophoretic grids were analyzed by using XRD (Rigaku Inc., DMAX-2500), and

**Table 1** Experimental conditions and tube inner diameters of the burner

| | Gas | | | | TTIP evaporation temperature |
|---|---|---|---|---|---|
| | Ar | $H_2$ | $O_2$ | Air | |
| Function | TTIP carrier gas | Fuel | Oxidizer | | 80 °C |
| Flowrates (L/min) | 0.3 | 2.0 | 3.7 | 30.0 | |
| Tube inner diameter (mm) | 3.9 | 16.6 | 70.0 | | |

the particle characteristics by using FE-SEM (Hitachi Inc., S-4700).

On the basis of the XRD analysis, the synthesis condition for the anatase-phased $TiO_2$ nanoparticles was selected. The formed nanoparticles were collected on the thermophoretic plate. Then, to investigate their thermal stability, the collected anatase nanoparticles were heat-treated at 600, 800, 1,000, and 1,200 °C for 30 min and 3 h, respectively. To analyze the activity of the photocatalyst, the degradation of organics, that is, methylene blue, by the heat-treated $TiO_2$ anatase nanoparticles was tested with UV light (1× 4 W, 365 nm, UVItec LF-204) irradiation. The initial concentration of methylene blue solution was $2.0 \times 10^6$ μg/m$^3$ (153 ppm), and the solution was sampled to measure the concentrations every 15 min. The concentration of $TiO_2$ nanoparticles was $1.6 \times 10^8$ μg/m$^3$. To measure the concentrations in the spectrometer (Spectronic, Genesys2), the sampled solutions were centrifuged (Hanil, MF-80) for 30 min at 4,000 rpm. To compare the photocatalytic ability of the flame-synthesized nanoparticles, the same degradation procedure was done with well-known commercial $TiO_2$ nanoparticles (P-25, Degussa).

## Results and discussion

The oxygen content in the oxidizer mixture was about 29.7 vol.%, as given in Table 1. The maximum temperature was measured to be 1,743 °C at 60 mm H.A.B. In our previous study [14], we reported that most of the formed nanoparticles were of anatase-phase having diameters ranging from 30 to 60 nm for the similar experimental condition.

Figure 1 shows the SEM images of the commercial P-25 $TiO_2$ nanoparticles, without heat-treated (a), and heat-treated at 600 °C (b) and 800 °C (c) for 30 min, respectively. Base on these images, the sintering of the P-25 nanoparticles was occurred at the temperature between 600 and 800 °C. But in the case of the flame-synthesized $TiO_2$ nanoparticles, as shown in Fig. 2, the sintering of the particles was occurred at higher temperature than that of P-25. Figure 2 shows the SEM images of the flame-synthesized $TiO_2$ nanoparticles, without heat-treated (a), and heat-treated at 600 °C (b), 800 °C (c), 1,000 °C (e), and 1,200 °C (f) for 30 min, and heat-treated at 800 °C (d) for 3 h, respectively. Comparing the particles in Fig. 2c, flame-synthesized particles heat-treated at 800 °C for 30 min, with those in Fig. 1c, P-25 particles heat-treated at 800 °C for 30 min, the sizes and shapes of the flame-synthesized particles were not changed significantly. While the heat-treatment temperature was 600 °C, there were no changes in the particle shape and size for both cases. But in case of 3 h heat-treatment at 800 °C of the

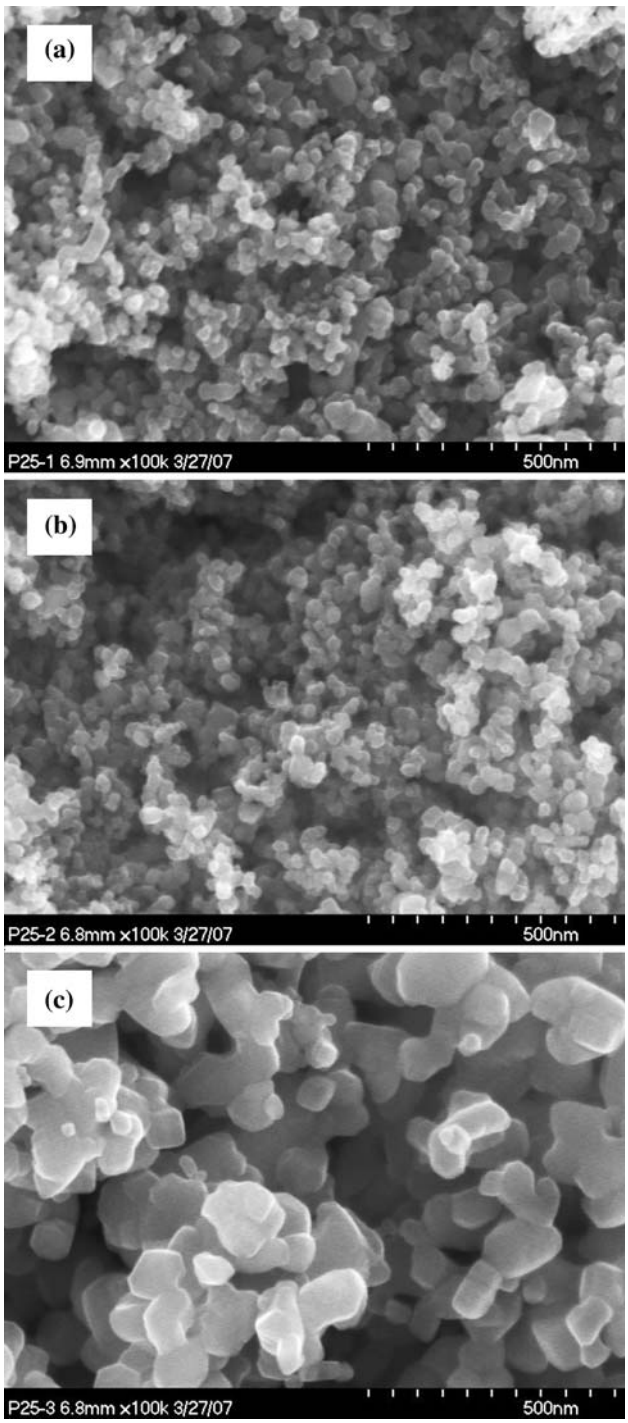


**Fig. 1** SEM images of non-heat-treated and heat-treated commercial P-25 $TiO_2$ nanoparticles, without heat-treated (**a**), and heat-treated at 600 °C (**b**) and 800 °C (**c**) for 30 min, respectively

flame-synthesized particles, Fig. 2d, some particles were sintered with each other and larger particles were formed.

The XRD patterns for the commercial and flame-synthesized particles are plotted in Figs. 3 and 4, respectively. As shown in Fig. 3, the commercial P-25 particles changed from anatase to rutile when the heat-treatment

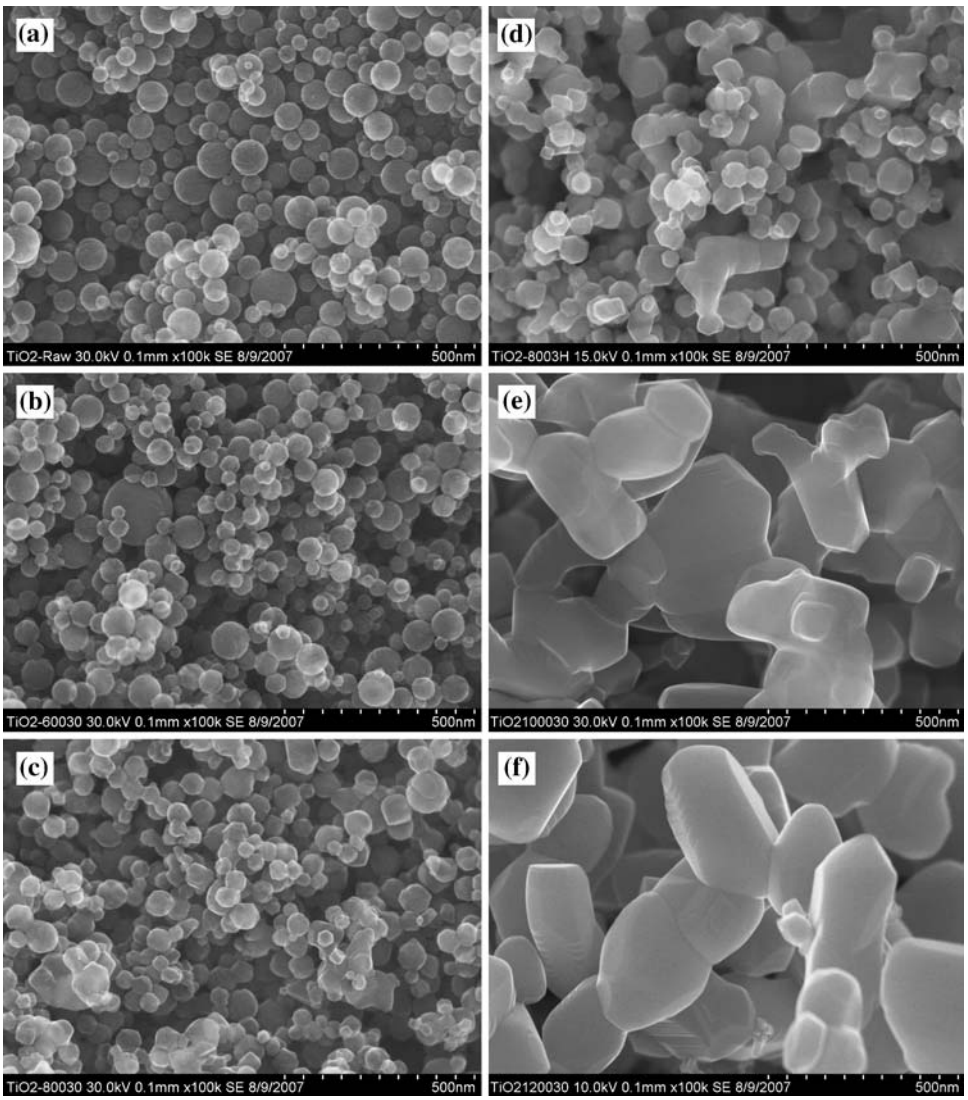


**Fig. 2** SEM images of non-heat-treated and heat-treated flame-synthesized $TiO_2$ nanoparticles, without heat-treated (**a**), and heat-treated at 600 °C (**b**), 800 °C (**c**), 1,000 °C (**e**), and 1,200 °C (**f**) for 30 min, and heat-treated at 800 °C (**d**) for 3 h, respectively

temperature was between 600 and 800 °C. The fractions of anatase-phased particles calculated from Spurr and Myers [20] decreased from 83.1 to 2.9%. But, as shown in Fig. 4, the flame-synthesized particles showed no significant changes in the XRD patterns at heat-treatment temperatures between 600 and 800 °C. The anatase fractions were almost same, about 96%. But in the cases of 1,000 and 1,200 °C, all the particles transformed to rutile-phase. Also, Fig. 5 shows similar result for the flame-synthesized particle when the heat-treatment lasted for 3 h. The anatase fraction of the case of 800 °C was decreased to 46.6%.

On the basis of the results related with the SEM images and XRD patterns, it is believed that the flame-synthesized $TiO_2$ nanoparticles are thermally more stable for heat-treatment at 800 °C than P-25 particles.

To verify the photocatalytic ability of the two types of nanoparticles, methylene blue was degraded with UV light irradiation. Figure 6 shows the photocatalytic reactions by the raw, 600°C, and 800°C heat-treated P-25 nanoparticles. As shown in the SEM images (Fig. 1) and XRD patterns (Fig. 3), the photocatalytic ability of P-25 particles heat-treated at 600 °C was almost same as that of the raw P-25 particles. But in the case of particles heat-treated at 800 °C, the degradation rate was much lower than those of the others. The results from the same procedure using the flame-synthesized $TiO_2$ nanoparticles are shown in Fig. 7. Different from the degradation rates of Fig. 6, those resulting from the two types of heat-treated (at 600 and 800 °C) flame-synthesized particles were higher than that by the non-heat-treated particles. As shown already in the

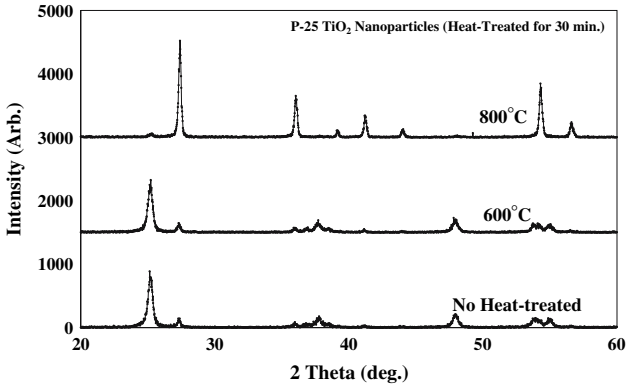


**Fig. 3** X-ray diffraction patterns of the heat-treated (30 min) commercial P-25 $TiO_2$ nanoparticles

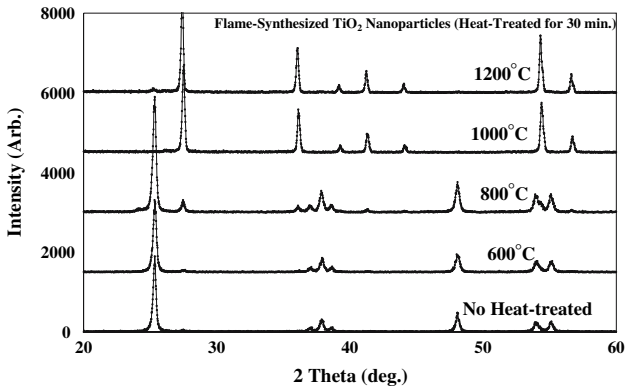


**Fig. 4** X-ray diffraction patterns of the heat-treated (30 min) flame-synthesized $TiO_2$ nanoparticles

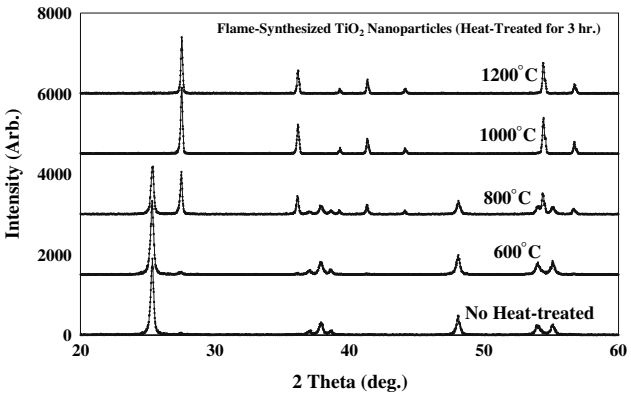


**Fig. 5** X-ray diffraction patterns of the heat-treated (3 h) flame-synthesized $TiO_2$ nanoparticles

SEM images and XRD patterns, there were no significant changes in the shape and crystalline phase between raw and these two types of heat-treated flame-synthesized particles. It is believed that MB decomposition rates by the heat-treatment were improved by the vaporization of water in

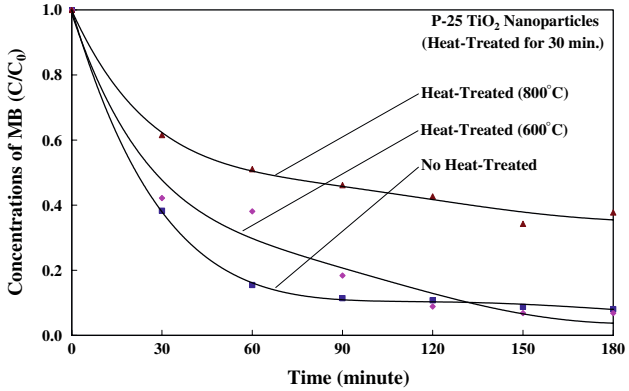


**Fig. 6** Normalized degradation of methylene blue concentrations by the commercial P-25 $TiO_2$ nanoparticles

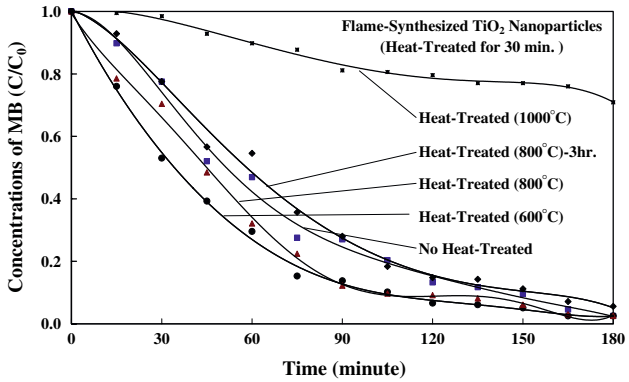


**Fig. 7** Normalized degradation of methylene blue concentrations by the flame-synthesized $TiO_2$ nanoparticles

the raw flame-synthesized particles. The vaporization of moisture in the $TiO_2$ sample means that the same amount of $TiO_2$ particles as the vaporized water can be put into the methylene blue solution additionally. That is, in the case of heat-treated particles, more $TiO_2$ particles were used to decompose the MB at the same weight as the case of non-heat-treated particles.

On the basis of the SEM images (Fig. 2), XRD patterns (Figs. 3 and 4), and MB degradation curves (Figs. 6 and 7), it is believed that the flame-synthesized $TiO_2$ nanoparticles are thermally more stable than the commercial P-25 nanoparticles when the heat-treatment temperature is 800 °C.

## Conclusions

In this article, we investigated the thermal stability of the flame-synthesized $TiO_2$ nanoparticles by examining the crystalline structures of these particles and by analyzing the photocatalytic degradations of methylene blue solutions. Also the results of thermal stability were compared with those of commercial P-25 nanoparticles. After

heat-treatment at 800 °C, the shapes and crystalline phases of the flame-synthesized $TiO_2$ nanoparticles showed no significant changes. In the case of commercial particles, most of the particles sintered with each other and changed to rutile-phase particles. The photocatalytic ability of heat-treated commercial particles degraded. On the contrary, the photocatalytic ability of the flame-synthesized particles improved. On the basis of the improved result of the photocatalytic degradation of methylene blue by use of the heat-treated flame-synthesized nanoparticles, it is believed that the flame-synthesized $TiO_2$ nanoparticles have higher thermal stability at 800 °C than the commercial P-25 nanoparticles.

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