

Synthesis of TiO₂ nanoparticles using titanium tetraisopropoxide and starch

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Simple synthesis of nanocrystalline titanium dioxide (TiO₂) by impregnation method was investigated. Titanium tetraisopropoxide (TTIP) was used as the precursor and starch as the impregnations matrix. TiO₂ nanoparticles of 100 nm in size were synthesized by varying the conditions. Crystallization and the growth of the particles were accelerated with increasing calcination temperature and time. The X-ray diffraction study shows that the product has anatase crystal structure at calcination temperatures below 600 °C. Anatase phase and rutile phase coexisted at 700 °C. At temperatures above 700 °C, the intensity of the anatase crystal phase peaks decreased and a peak of the new rutile crystal phase appeared at 2θ of 27.42(110), 36.11(101), 41.28(111) and 55.06(220). In more than 800 °C of temperature, rutile phase only existence.

Key words: TiO₂, Starch, Nanoparticle.

Introduction

There are about 11 types of titanium dioxide crystals as such as anatase, rutiles, and brookite etc. Of these, anatase, rutile and brookite are the best formed and exhibit excellent features. Titanium dioxide is highly oxidizing, harmless to the human body, and very stable. In addition, the band gap energy is about 3 eV, which is the optical semiconductor characteristic [1]. TiO₂ particles with excellent electrical, magnetic, catalytic, electrochemical and optical properties are used in various industrial fields [2-5]. TiO₂ has a very high refractive index and is excellent in whiteness, and thus is used for the preparation of white pigments and various pigments. In particular, ultraviolet light absorbing ability is excellent in the ultraviolet wavelength range of 400 nm or less, and it is chemically stable and used as a UV blocking agent [6, 7]. In addition, due to the characteristics of ultrafine particles, it has a large specific surface area, strong durability, and excellent photocatalytic ability and is used in various catalysts, catalyst supports, sterilizing media, and sensors [8-12]. We have previously reported the synthesis of titanium oxide nanoparticles using pulp as the impregnation matrix [13-15]. In this synthetic method, a polymer material having a microfibril structure is impregnated with a metal salt, and then the impregnated mixture is dried and fired to prepare ceramic nanoparticles. This method can control the particle size by changing the type of the impregnation medium, the heat treatment

conditions, and the concentration of the aqueous metal salt solution [16]. It is also suitable for the synthesis of ceramics nanoparticles with a uniform particle size distribution in a simple process without using the alkaline organic solvent used in the precipitation method [17]. In this study, impregnation method was selected as a method for synthesizing titanium oxide nanoparticles. Titanium tetraisopropoxide (TTIP) was used as the starting material of this synthesis method, and starch was used instead of pulp as the impregnation matrix. We chose Starch as a matrix because starch is economically advantageous because of its simpler manufacturing process than industrial pulp. Pulp is manufactured in paper mills, which requires a lot of wood to get 1 kg of pulp. On the other hand, Starch can be obtained directly by grinding grain or plant. Starch in powder form can be impregnated more than pulp because it has a larger surface area than plate-type industrial pulp. As a result, yields can be increased and economic processes can be developed. Pulp having a plate-like dense and rigid structure has a problem that TTIP is not completely impregnated. Starch in powder form, however, does not have this problem. Starch with fine particles and large surface area is easy to impregnate with TTIP. On the other hand, Starch is not easy to impregnate with aqueous solution. Starch dissolves in water to a certain extent and agglomerates into a massive mass, which is inconvenient for drying and firing operations.

Experimental

Titanium tetraisopropoxide (TTIP, ≥95.0%), isopropanol (C₃H₈O, ≥99.7%) and starch (C₆H₁₀O₅)_n, ≥99.5%) were purchased Dae Jung Chemical Co. All the chemical

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Fig. 1. Preparation procedures of TiO_2 nano powders.

reagents were analytically pure and used without further purification. The precursor solution was 5 mL of TTIP mixed with 25 mL isopropanol under a vigorous stirring. Schematic diagram of the TiO_2 nanoparticles prepared by this method is shown in Fig. 1. The starch and TTIP

precursor solution were impregnated at a weight ratio of 1:1. The impregnated precursor was dried at 120 °C for 3 hours. The dried precursor was calcined in an electric furnace at 500 °C for 1 hour to remove the organic components in the precursor and the starch. This calcined sample was pulverized with agate and then calcined in an electric furnace at a temperature range of 600 °C and 1,000 °C (heating rate:5 °C/min) for 1 to 3 hours. The calcined samples were pulverized to obtain final powdery TiO_2 . X-ray diffraction pattern was investigated by DMAX-2200V/PC High power X-ray diffractometer of Rigaku. Cu-K α with a Ni filter was used to measure a scanning speed of 5°/min, an acceleration voltage of 40 kV, and an acceleration current of 30 mA in a diffraction angle (2θ) range of 10 to 80°. FE-SEM (Model S-4300, Hitachi, Acceleration Voltage 17 kV) was used for surface structure analysis such as the particle size of the prepared TiO_2 powder.

Results and Discussion

Fig. 2 shows the XRD diffraction pattern of TiO_2 powder calcined at 500-800 °C for 1 hour, respectively. As shown in Fig. 2(a) and (b), the XRD diffraction patterns of powders prepared at 500 °C and 600 °C showed only an anatase crystalline form. In these samples, diffraction peaks of the anatase crystal form were found at the 2θ values of 25.3, 37.9, 48.1, 53.9, 55.0, 62.8, 68.9, 70.41 and 75.18, and the corresponding Miller indices were (101), (004), (211), (204), (116), (220), and (215). When the calcination time was

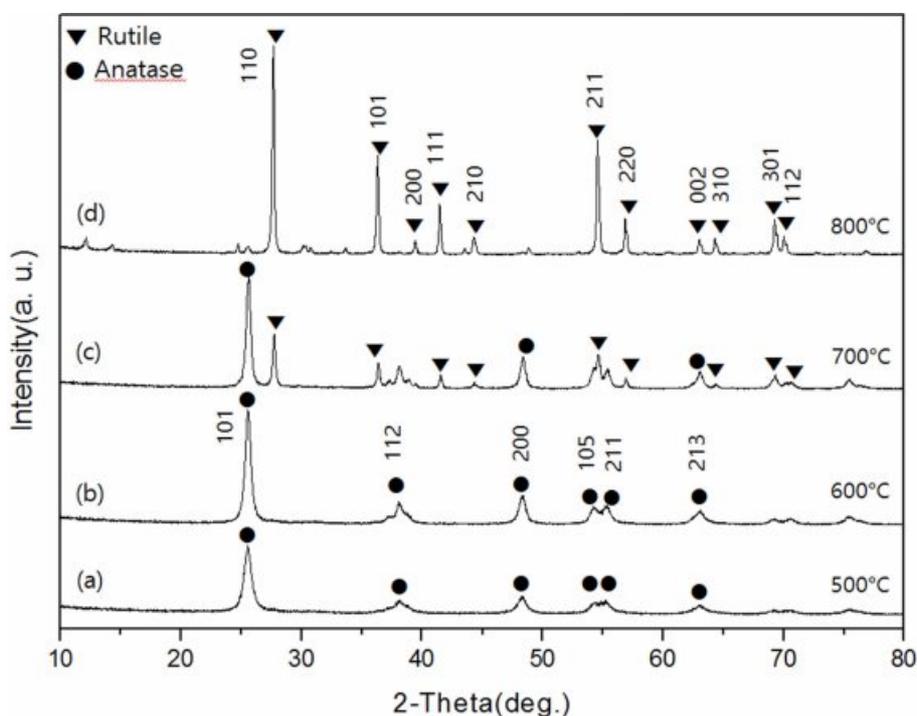


Fig. 2. XRD patterns of TiO_2 powders in various calcination temperatures for 1 hr.

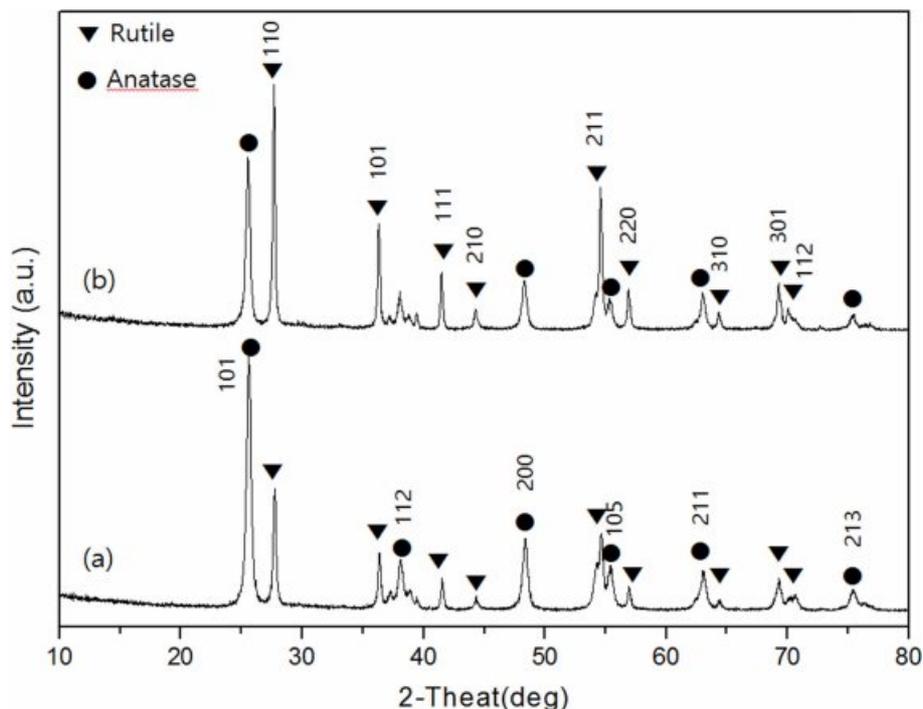


Fig. 3. XRD patterns of TiO_2 powders at $700\text{ }^\circ\text{C}$ at various calcination time (a) 1 hr and (b) 3 hr.

increased from 1 hour to 3 hours in this temperature range, the size of the crystals increased. However, the crystal phase did not change and only anatase phase appeared. On the other hand, in the XRD diffraction pattern of the calcined powder at $700\text{ }^\circ\text{C}$ shown in Fig. 2(c), anatase phase and rutile phase existed together. At this time, the intensity of the diffraction peak of the anatase phase was lower than that of the calcined powder at $600\text{ }^\circ\text{C}$, and the diffraction peak newly appeared at the 2θ value of $27.42(110)$, $36.11(101)$, $41.28(111)$ and $55.06(220)$ are due to the formation of the rutile crystal form[13]. In the diffraction pattern of samples prepared at $800\text{ }^\circ\text{C}$ with increasing calcination temperature, only rutile phase, which is a crystalline form at high temperature, appeared. Fig. 3 shows the XRD diffraction pattern of the samples prepared by different calcination times of 1 hour and 3 hours at $700\text{ }^\circ\text{C}$. Both the anatase phase and the rutile phase exist in Fig. 3(a) and (b). Therefore, it was found that there existed two crystal phases regardless of increase of calcination time at $700\text{ }^\circ\text{C}$. The calcination time increased to 3 hours Fig. 3(b), the diffraction intensity of the anatase peak is weakened. At $600\text{ }^\circ\text{C}$, the change in the crystal phase, which did not occur even when the calcination time was increased, appeared only at $700\text{ }^\circ\text{C}$. As a result, the transition temperature of the crystal phase was $700\text{ }^\circ\text{C}$. Therefore, it can be seen that the calcination temperature has a greater influence on the crystal phase transition than the calcination time. On the other hand, in Fig. 3(b) where the calcination time was increased to 3 hours, the peak of the anatase crystal

phase exhibited lower strength than that of Fig.3 (a) when the calcination time was 1 hour. This suggests that the calcination time has some influence on the transition phase. As a result, it was confirmed that the anatase crystal phase was obtained at a synthesis temperature of $600\text{ }^\circ\text{C}$ or lower, and the rutile phase was formed at a synthesis temperature of $700\text{ }^\circ\text{C}$ or higher. The reason why the crystal phase differs according to the synthesis temperature is that the surface energy changes depending on the particle size. Since the surface energy of anatase phase particles is less than the surface energy of rutile particles, they are synthesized at lower temperatures. In our earlier work, when pulp was used as the impregnation matrix, anatase phase and rutile phase appeared at a calcination temperature of $600\text{ }^\circ\text{C}$. There was a difference in the crystalline phase as the impregnated matrix changed from pulp to starch. That is, when a pulp was used, a rutile phase was obtained at a temperature lower by $100\text{ }^\circ\text{C}$. This is because micro-morphology of pulp and starch are different. Starch produces more heat energy than pulp when burned. Thus, when starch is used as a matrix, more heat energy is transferred to the precursor TTIP. It is believed that TTIP is decomposed at a lower temperature, and TiO_2 has a lower production temperature. Fig. 4(a) shows the EDX spectra of samples calcined at $800\text{ }^\circ\text{C}$ for 1 hour. The elemental peaks corresponding to titanium and oxygen were found, and the distribution of these two elements was found to be in the form of TiO_2 by calculating the stoichiometry ratio. Fig. 4(b) and (c) shows SEM photographs of samples calcined at $700\text{ }^\circ\text{C}$ for 1 hour and 3 hours,

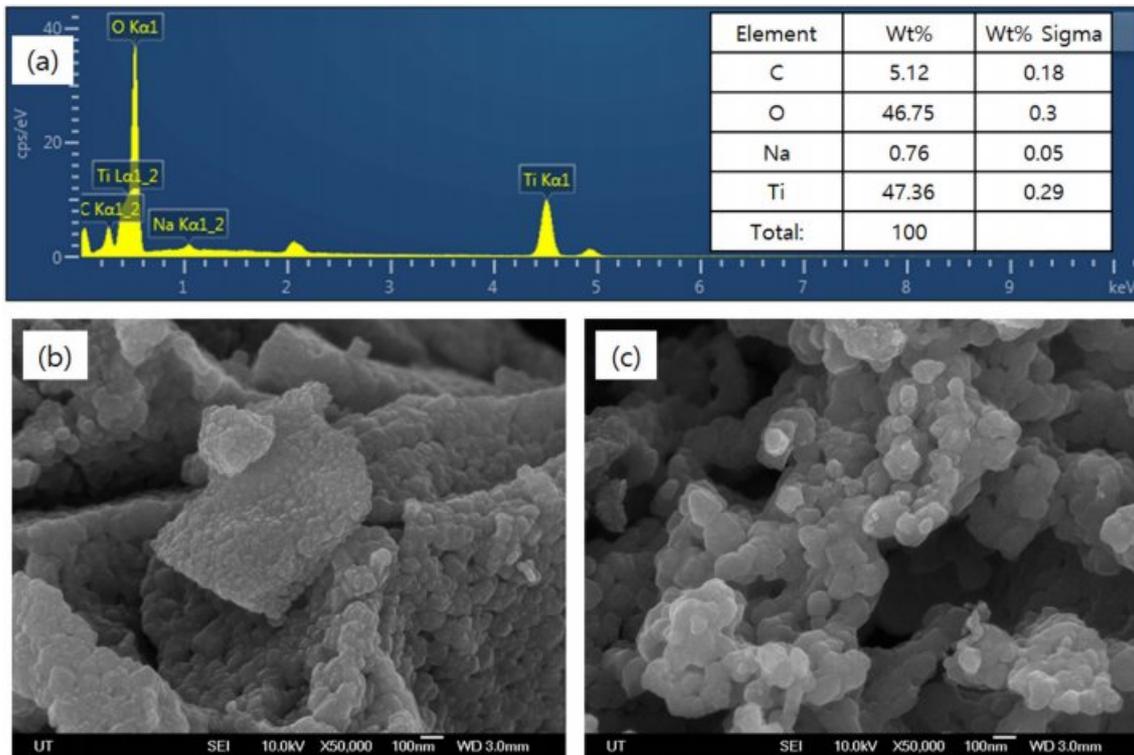


Fig. 4. EDX and FE-SEM images of TiO_2 powders in various calcination conditions: (a) 800 °C, 1 hr, (b) 700 °C, 1 hr, and (c) 700 °C, 3 hrs.

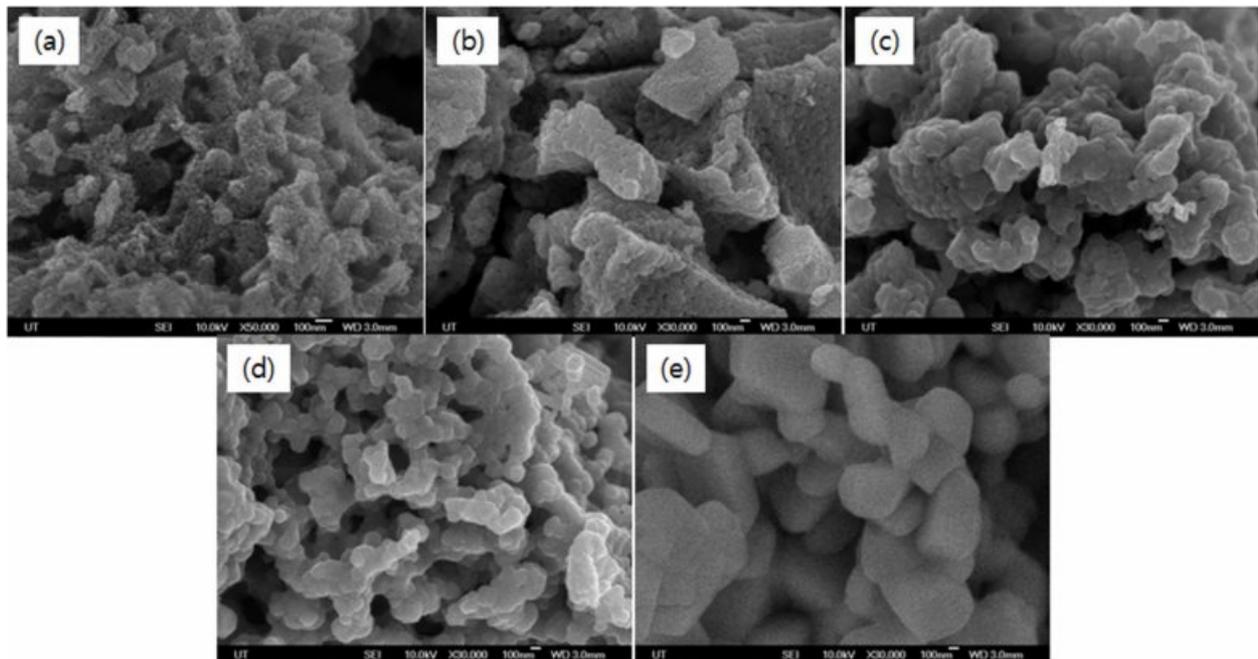


Fig. 5. FE-SEM images of TiO_2 powders at various calcination temperatures for 1 hr: (a) 600 °C, (b) 700 °C and (c) 800 °C, (d) 900 °C and (e) 1,100 °C.

respectively. As can be seen in the figure, crystals grow as the calcination time increases. Fig. 5 shows the results of FE-SEM measurement of the morphology of synthesized TiO_2 particles when the calcination time was fixed to 1 hour and the calcination temperature

was changed from 600 °C to 1,100 °C. The samples calcined at 600 °C showed very small particle size (≤ 50 nm). Since the anatase phase is more stable than the rutile phase as the particle size is smaller, crystals of the anatase phase are formed only at a low calcination

temperature of 600 °C or lower (Fig. 2 (a)). In the samples calcined at 700 °C, grain growth (≤ 100 nm) began to be observed with increasing crystallinity. In the samples calcined at 800 °C, the shape and size of the particles grew to more than 100 nm, and crystallization progressed over a wide range and uniform particle size distribution began to appear. At the calcination temperature of 900 °C to 1,100 °C, the growth of the particles is promoted, and the phenomenon of crystal growth (≥ 100 nm) is observed. The crystallization of the particles was promoted at 1,100 °C, and the rutile-phase TiO₂ crystal was clearly identified.

Conclusions

TiO₂ nanoparticles were synthesized under various conditions by impregnation method. TTIP was used as the precursor and starch as the impregnations matrix. As a result of XRD analysis, only anatase phase was formed when calcined at 500-600 °C. At 700 °C, the anatase phase and the rutile phase existed together. At 800 °C and above, only the rutile phase existed. TiO₂ with a size of 100 nm or less were obtained when calcined for 1 hour at 700 °C. As a result of firing at 600-800 °C for 1-3 hours with different calcination conditions, crystallization was promoted and grain size was increased with increasing calcination temperature and time.

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