Characterization of TiO₂ Synthesized in Acidic Conditions at Low Temperature by Sol-gel Method

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Abstract  Titanium dioxide (TiO₂), which is one of the most basic materials in our daily life, plays a key role for environment purification. We synthesized TiO₂ nanoparticles by the hydrolysis reactions of titanium tetraisopropoxide using HNO₃ as a peptizing agent or CH₃COOH as a chelating agent in the sol-gel method. The powder consisted of a rod shape or a spherical shape according to the concentration and kind of acid. The physical properties of TiO₂ nanoparticles were investigated with X-ray diffraction, SEM, BET analysis, and UV-Vis spectrophotometer.

Keywords : TiO₂, Nanoparticles, Photocatalyst, Sol-gel procedure

1. Introduction

TiO₂ nanoparticles have attracted much interest from many researchers due to their wide applications such as the white pigment, sensors, catalysts, and photocatalysts. TiO₂ photocatalysts have been extensively used for environmental applications because of its high oxidative power, nontoxicity, photostability, and water insoluble properties under most conditions [1-7]. TiO₂ with a controllable size distribution and morphology has been obtained by using sol-gel process methods. The chemistry of the sol-gel process is mainly based on hydrolysis (1) and polycondensation (2, 3) of titanium alkoxides leading to the formation of an extended network [3].

\[
\begin{align*}
\text{Ti–OR} + \text{H}_2\text{O} &\rightarrow \text{Ti–OH} + \text{ROH} \quad (1) \\
\text{Ti–OH} + \text{OR–Ti} &\rightarrow \text{Ti–O–Ti} + \text{ROH} \quad (2) \\
\text{Ti–OH} + \text{OH–Ti} &\rightarrow \text{Ti–O–Ti} + \text{H}_2\text{O} \quad (3)
\end{align*}
\]

The morphologies and crystal phase of the resulting product derived from the sol-gel process are strongly affected by kinetics of hydrolysis and condensation reactions of alkoxide precursor, chemical compounds, and experimental conditions [3]. The basic requirements for photoactive materials are high crystallinity, large surface area, and higher concentration of surface hydroxyl group, etc [8, 9]. The crystalline TiO₂ synthesized at low temperature will be able to give many noticeable advantages. For instances, this preparation method allows a wider selection of support materials such as plastic, wood, or cotton. It will offer a benefit for the control of the crystal size and for the fine nanocrystalline. This method also saves energy and overall cost during the TiO₂ preparation process. It can be a practical preparation method. The various techniques using sol-gel method have been applied to produce TiO₂ powder [2-5].

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In this work, the physical properties of TiO$_2$ synthesized in acidic conditions at the mild reaction temperature were analyzed. TiO$_2$ nanoparticles consisted of anatase, rutile, or anatase and rutile mixed phase. The TiO$_2$ preparation process at low temperature can allow not only the simple and economic synthesis method but also the responsible TiO$_2$ product with larger surface areas.

2. Materials and Experimental

The sol-gel process was carried out using titanium tetraisopropoxide (TTIP) (98%, Sigma-Aldrich Chemicals Ltd., USA), isopropyl alcohol (IPA) (99.5% anhydrous, Sigma-Aldrich Chemicals Ltd., USA), HNO$_3$ (Dae Jung Chemical Co., Korea), CH$_3$COOH (Dae Jung Chemical Co., Korea), and distilled water. The molar ratio of materials and the name of samples are listed in Table 1. The solution A with TTIP and IPA and the solution B with H$_2$O and acid were mixed in ambient conditions for 50 hours and then heated at 80°C for 10 hours. After separating and several washing with ultrasonic wave, TiO$_2$ powder was dried at 100°C.

Table 1 summarizes the molar ratio of the materials. In the case of H1 sample, the molar ratio of TTIP, IPA, H$_2$O, and HNO$_3$ was 1, 1, 100, and 0.1, respectively. When we changed the molar ratio of HNO$_3$ acid, we obtained H2, H3, H4, and H5 samples. Similarly, we obtained C1, C2, C3, and C4 by changing the molar ratio of CH$_3$COOH acid.

The X-ray diffraction (XRD, Rigaku ultra-X, Rigaku Co., Cu K$_\alpha$ radiation, 40 kV, 120 mA, Japan) patterns of TiO$_2$ powder were measured at step scan rate of 0.02°/sec in the 2θ range (10-80°) to identify the crystalline phase of TiO$_2$. The morphologies were analyzed using scanning electron microscopy (SEM, Supra 40, Carl Zeiss Co., Ltd., Germany). The absorption spectra were recorded on UV-Vis spectrophotometer (OPTIZEN POP, Mecasys Co., Ltd., Korea) using the normal incident transmittance. The specific surface areas were calculated by BET method (nanoPOROSITY-XQ, Mirae Scientific Instruments Co., Korea).

3. Results and Discussion

Fig. 1 shows the TiO$_2$ phase variation of the X-ray diffraction patterns according to the different molar ratio of HNO$_3$ acid. As increasing amount of HNO$_3$ acid, the anatase phase changed into the rutile phase. The phase of H1 sample was confirmed to be primarily anatase phase. H2 sample is intermediate period of the changed process. H3 sample had only the rutile phase. However, the peaks of the sample H4 showed not only the rutile phase but also the anatase phase. Therefore, the concentration of acid may be

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<th>Table 1. The molar ratio of the starting materials</th>
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Fig. 1. X-ray diffraction patterns of TiO$_2$ prepared using HNO$_3$ (A : Anatase phase, R : Rutile phase, B : Brookit phase).
limited at 1.5 molar ratio. We continuously increased HNO₃ acid to 2.0 molar ratio. The phase of H5 sample was similar to H4 sample. It demonstrated that there is a limited concentration of HNO₃ acid. Some research results showed about the stable properties of rutile TiO₂ phase, especially, rutile phase with nanorod morphology [5, 8-11].

Fig. 2 shows the X-ray diffraction patterns of TiO₂ powder synthesized in the different molar ratio of CH₃COOH and shows all samples have only anatase phase. Fig. 2 indicates that the concentration of CH₃COOH acid do not affect to the phase of TiO₂.

![Fig. 2. X-ray diffraction patterns of TiO₂ prepared using CH₃COOH.](image)

![Fig. 3. SEM images of TiO₂ prepared using HNO₃ ((a) H1, (b) H2, (c) H3, (d) H4, and (e and f) H5).](image)
Fig. 3(a) shows the surface of H1 powder with about 10 nm particle size. When the molar ratio of HNO₃ acid was increased to 0.5, the surface of the obtained H2 powder became uniform form. H3 powder shows the nanorod shape with about 50 nm length and 20 nm diameter, as shown in Fig. 3(c). This is similar to the results of other methods [8, 9, 11]. However, the reaction time and the reaction temperature were more short and low when we compared to other methods [9, 11]. In H4 sample, the particles were aggregated to create particles with larger size. Especially, Fig. 3(e) and 3(f) show the surface of H5 powder with irregular surface morphologies. The very small particles were observed along with the large particles aggregated in some areas of H5 sample. When we increased the molar ratio of HNO₃ acid, the size of TiO₂ particles and the degree of aggregation were also increased.

Fig. 4 shows the surface of TiO₂ powder with regular morphology. The size of particles was about 10 nm. The surface of TiO₂ prepared using CH₃COOH was smooth. However, the surface had some points where particles are agglomerated. Fig. 4 shows that the concentration of CH₃COOH does not affect to the surface of TiO₂.

Fig. 5 shows the nitrogen adsorption-desorption isotherms for TiO₂ prepared using HNO₃.
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[12], H1 sample exhibited a typical type II isotherm and type E hysteresis loops which are attributed to the existence of ink-bottle type pores and mesopores. Other samples have the narrow pores or the narrow slit-like pores because loops of the samples were very small and narrow. The BET surface areas of H1, H2, H3, H4, and H5 were 174.29, 181.15, 129.54, 198.73, and 136.86 m$^2$/g, respectively. These surface areas are larger than the results of previous methods [4, 5, 10].

Fig. 6 shows the nitrogen adsorption-desorption isotherms for TiO$_2$ powders prepared using CH$_3$COOH acid. All samples indicated isotherm type IV. The hysteresis loops in the adsorption-desorption curve indicate that C1, C2 and C4 sample had type E hysteresis loop that can be attributed to “ink-bottle” pores. C3 sample showed the narrow hysteresis loop caused by its particle arrangement with a narrow pore size. The BET surface areas of C1, C2, C3, and C4 were 243.80, 229.72, 265.53, and 256.27 m$^2$/g, respectively. This results are similar to that of SEM and X-ray diffraction. These surface areas are also larger than the results of previous methods [4, 6, 11].

Fig. 7 shows the UV-Vis absorption spectra of TiO$_2$ using HNO$_3$ acid. The absorption edge occurred below the wavelength of 350 nm. When we increased the concentration of HNO$_3$ acid, the second peak was decreased. However, the second peak of H2 was higher than that of H1 peak because H2 is an intermediate stage changing from anatase to rutile phase.

Fig. 8 shows the UV-Vis absorption spectra of TiO$_2$ prepared using CH$_3$COOH acid. The absorption edge is similar to that of TiO$_2$ using HNO$_3$ acid. The absorption results showed the similar pattern for all samples because of their same properties with anatase phase.

4. Conclusions

A sol-gel method with acid hydrolysis was applied to synthesize TiO$_2$ nanoparticles and to grow TiO$_2$ crystal phase at low temperature. The hydrolysis process was carried out at room temperature for 50
hours and at 80°C for 8 hours in the various concentration of HNO₃ or CH₃COOH acid in order to achieve the fine nanocrystalline TiO₂. The results of the X-ray diffraction analysis showed that H1 sample had mainly the anatase phase whereas H3 sample had only the rutile phase. The physical properties of C1 sample was similar to that of C2 and C4 sample when compared with the results of SEM and UV-Vis spectrum but C1 sample had the larger surface area compared to the surface area of C2 and C4. C3 sample had the largest surface area originated from their regular TiO₂ particles array. In future work, we will investigate the degradation efficiency of methylene blue containing TiO₂ powder under UV irradiation.

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References