Synthesis and Characterization of Titania–Sugar Alcohol Complex Nanoparticles

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Abstract: Complexes between TiO$_2$ and sugar alcohol molecules or polyol molecules were prepared by heating the mixture of titanium isopropoxide (TIP) and ethylene glycol, glycerin, meso-erythritol, or D-mannitol aqueous solutions at 368 K for 24 h. The degree of crystallization of TiO$_2$ in the obtained TiO$_2$–sugar alcohol or polyol complex depended on the concentration of the polyol and sugar alcohol aqueous solution. When the TiO$_2$–sugar alcohol or polyol complex was prepared by using the same concentration of the sugar alcohol or polyol aqueous solution, the degree of crystallization of the TiO$_2$ in the complex decreased with increase in the number of OH groups per molecule. According to the results of the DTA measurements and the element analysis, the strength of the interaction between Ti$^{4+}$ ions and polyol or sugar alcohol molecules increased with increases in the number of OH groups in the molecules. The heat treatment of TiO$_2$–D-mannitol complex in 0.5 mol/l HNO$_3$ aqueous solution at more than 318 K enabled to obtain TiO$_2$–D-mannitol complex nanoparticles by breaking the bond between the D-mannitol molecules and Ti$^{4+}$ ions. The obtained TiO$_2$–D-mannitol complex nanoparticles had large surface area which was more than 300 m$^2$/g and showed photocatalytic activity. Furthermore, the complex nanoparticles can be dispersed into the distilled water with high stability.

Key-words: Titanium oxide, Photocatalyst, Nanoparticles, Stable sol

1. Introduction

Titanium dioxide (TiO$_2$; titania) is an n-type oxide semiconductor and shows photocatalytic activity and photoconductiveivity. Furthermore, the application of dye-sensitized anatase-type TiO$_2$ nanoparticles for solar cell photovoltaic-chemical systems has also been intensively investigated. The control of the particle size and morphology of titania (TiO$_2$) particles is required for the control of the optical and catalytic properties of the TiO$_2$ particles. A stable sol with the homogeneous dispersion of the TiO$_2$ nanoparticles can be used for low temperature preparation of the TiO$_2$ thin films and the precursor of multicomponent oxides containing Ti such as BaTiO$_3$. The mixing of sols easily produces the homogeneous mixture of the component oxide nanoparticles.

The complex formation between TiO$_2$ and organic molecules enables to control the surface characteristics of oxide nanoparticles, which greatly affect their reactivity, sinterability, and the dispersion characteristics in a solution. If a small amount of organic molecules can improve the characteristics of TiO$_2$ nanoparticles effectively, the formation of the TiO$_2$–organic complex nanoparticles contributes to improve the photocatalytic activity of TiO$_2$ nanoparticles due to their homogeneous dispersion in a solution. In particular, the TiO$_2$–organic dye complex have been intensively investigated as the electrode of dye sensitized solar cells. The formation of the complex between TiO$_2$ and organic molecules is useful techniques to control the characteristics of TiO$_2$ nanoparticles.

A polyol molecule that has more than four hydroxyl groups is assigned to sugar alcohol since they are obtained by reduction of the sugar molecule. Oakey et al. have shown that a small amount of sugar alcohol molecules effectively stabilizes silica sols due to coordination and adsorption of the sugar alcohol molecules on the silica surface. In particular, the sugar alcohol molecules can coordinate to metal ions more effectively than diols and triols. In our previous study, the authors found that polyol molecules greatly affect the formation behavior of crystallized TiO$_2$ nanoparticles from Ti-peroxo complex. It was reported that the presence of alcohol molecules affects the oxidation and oxolation processes of the hydrolysis reaction of Ti$^{4+}$ by coordination of the alcohol molecules. Furthermore, sugar alcohol molecules are hydrophilic. Then, if TiO$_2$–sugar alcohol complex nanoparticles can be obtained, the stability of dispersion of the TiO$_2$ nanoparticles in an aqueous solution will be greatly improved. The stable sol with the dispersion of the TiO$_2$–sugar alcohol complex nanoparticles can be used for preparation of the TiO$_2$ photocatalyst films. Furthermore, if the hydrolysis reaction of alkoxides through the use of a small amount of sugar alcohols successfully forms the TiO$_2$–sugar alcohol complex, the degradation of the photocatalytic activity by the coexisting sugar alcohol molecules will be restrained and the advantage of using sugar alcohol complex will be effectively shown.

In this study, the effects of the sugar alcohol molecules on the hydrolysis reaction of Ti alkoxides were investigated, and...
the formation behavior of the TiO$_2$–sugar alcohol complex was examined. Furthermore, a novel synthesis method for TiO$_2$–sugar alcohol complex nanoparticles was examined utilizing the hydrolysis reaction of the TiO$_2$–sugar alcohol complex. The photocatalytic activity of the TiO$_2$–sugar alcohol complex nanoparticles was also investigated and the advantage of the TiO$_2$–D-mannitol complex nanoparticles were also examined.

2. Experiments

2.1 Preparation of the TiO$_2$–Sugar alcohol complex

TiO$_2$–polyol or the sugar alcohol complex was prepared as follows. First, 100 ml of an aqueous solution of polyl or sugar alcohol was added to the 0.01 mol/l of titanium tetraisopropoxide Ti(O–Pr)$_4$ (TIP) in a Pyrex glass beaker. At this point, a white precipitate was obtained. The polyols we used were ethylene glycol (HOCH$_2$CH$_2$OH) and glycerin (HOCH$_2$CH(OH)CH$_2$OH). The sugar alcohols were mesoerythritol (HOCH$_2$CH(OH)CH(OH)CH$_2$OH) and D-mannitol (HOCH$_2$CH(OH)CH(OH)CH(OH)CH$_2$OH) (M). The solution concentrations ranged from 0 mol/l to 5 mol/l. The mixed solution of TIP and polyl or sugar alcohol aqueous solution was heated at 368 K (95°C) for 24 h in a 200 ml Pyrex glass beaker capped with a rubber stopper. In order to remove the polyols and the organic compounds formed by the hydrolysis reaction of alkoxide, the obtained precipitate was centrifuged at 3000 r.p.m. for 5 min. The obtained precipitate was then dispersed into 100 ml of distilled water and centrifuged again. This washing process of the obtained precipitate was repeated three times. The obtained TiO$_2$–polyol or sugar alcohol complex precipitate was dried in air at 348 K for 12 h. All of the chemicals used in this preparation were of reagent grade (Wako Pure Chemical Industries, Ltd., Osaka).

2.2 Preparation of TiO$_2$–sugar alcohol complex nanoparticles

The 0.5 g of the TiO$_2$–D-mannitol complex prepared by heating of the mixture of TIP and 0.1 mol/l of D-mannitol aqueous solution was added to 100 ml of 0.5 mol/l HNO$_3$ aqueous solution. The solution with the complex powder was heated at 368 K, 348 K, 328 K, or 318 K for 24 h and the solution was obtained. In order to remove HNO$_3$ and other impurities in the obtained sol, 100 ml of 1 mol/l NH$_3$ aqueous solution was added to the sol. The TiO$_2$–D-mannitol complex nanoparticles in the sol precipitated and the solution with the precipitate was centrifuged at 3000 r.p.m for 5 min. The obtained precipitate was then dispersed into ethanol (EtOH) and centrifuged again at 3000 r.p.m for 5 min. The washing process was repeated three times. The obtained precipitate was then dispersed into 100 ml of distilled water. The precipitate was spontaneously dispersed in the distilled water, and the stable sol was obtained. The sol was dried at 348 K for 12 h in order to examine the shape and size of the particles in the sol.

2.3 Characterization

The X-ray diffraction (XRD) patterns of the samples were obtained by using Mac Science M18X–HF–SRA equipment. Cu was used as the target (Cu K$_\alpha$, 40 kV, 200 mA). An optical system of SS = 1’, DS = 1’, RS = 0.30 mm and a graphite monochromator were used. The particle shape was observed by a field emission–secondary electron microscope (FE–SEM, JSM–6330, JEOL, Inc., Tokyo). After pretreatment at 383 K in 1 mPa for 2 h, the N$_2$ adsorption isotherm was measured at 77 K by the volumetric method. In order to estimate the amount of organic compounds in the obtained TiO$_2$ powder, the carbon content was measured by elemental analysis (Perkin Elmer Co. Ltd. Model 2400). The error of the elemental analysis was 1% for each element. Differential temperature analysis (DTA) curves were measured at a heating rate of 10 K/min (TG/DTA300; Seiko Instruments Co., Ltd.).

The Ti$^{4+}$ concentration in the solution heated with titanium tetraisopropoxide Ti(O–Pr)$_4$ (TIP) and D-mannitol aqueous solution was measured by absorpimetric analysis with diantripyrmethane (C$_{11}$H$_{13}$N$_2$O$_2$). The aqueous solution of diantripyrmethane was added to the solution, and the absorbance at 560 nm was measured using a UV–VIS spectrometer (JASCO U–best210, Jasco, Inc., Tokyo, Japan). The Ti$^{4+}$ concentration in the solution was estimated from the absorbance at 560 nm.

2.4 Measurement of photocatalytic activity

The 200 ml of 1.5 × 10$^{-3}$ mol/l methylene blue (MB) aqueous solutions were prepared and 40 mg of a TiO$_2$ powder was added into the solution. The solution was stirred at 500 r.p.m. without UV irradiation for 30 min. The methylene blue concentration at this time was used as the reference concentration for estimation of the decomposed amount of methylene blue by photocatalytic activity since the adsorption equilibrium was almost established. The irradiation of the UV light (1 mW/cm$^2$ 320 nm–400 nm) was then started using black lights (National Co. Ltd., FLS20S). A cut-filter was not used. Three ml of the solution was separated by filtration with 0.45 µm membrane filter once per half hour. The absorbance of the corrected solution at 655 nm was measured by using an UV–VIS spectrometer (HITACHI UV2000). The concentration of methylene blue was calculated from the absorbance by using the working curve.

3. Results and discussion

3.1 Hydrolysis reaction of TIP with a polyol or a sugar alcohol aqueous solution

In the present study, the effects of sugar alcohol and polyol molecules on the hydrolysis reaction of TIP were examined. Figure 1 shows the XRD patterns of the powders prepared by heating the mixture of TIP and D-mannitol aqueous solution.
at 368 K for 24 h. D-mannitol is a sugar alcohol and one of the polyols with six OH groups per a molecule. When the 0.005 mol/l, 0.01 mol/l, and 0.02 mol/l concentrations of the D-mannitol aqueous solution were used for the hydrolysis reaction of TIP, anatase TiO$_2$ was obtained as shown in Figs. 1(a), (b), and (c). The half width of the XRD peaks increased with increases in the concentration of the D-mannitol aqueous solution. This result suggests that the crystallite size of the obtained anatase TiO$_2$ decreased with increases in the concentration of the D-mannitol aqueous solution. When concentrations were larger than 0.05 mol/l, the clear peaks were not observed in the XRD patterns shown in Figs. 1(d) and (e). This result indicates that the obtained TiO$_2$ was amorphous or their crystallite size was too small to appear the peaks in the XRD patterns when the concentration of D-mannitol aqueous solution was larger than 0.05 mol/l.

Figure 2 shows the XRD patterns of the powders prepared by heating the mixture of TIP and ethylene glycol aqueous solution at 368 K for 24 h. The XRD patterns in Figs. 2(a) – (c) can be assigned to anatase TiO$_2$. Thus, ethylene glycol did not affect the hydrolysis reaction of TIP or the crystallization process of TiO$_2$. It is considered that the number of OH groups in a polyol molecule is related to the strength of the coordination of polyol and sugar alcohol molecules to cations.

In order to investigate the effects of the polyol and sugar alcohol molecules on the degree of crystallization of the obtained TiO$_2$, the crystallite size was estimated by using Scherrer’s equation and the half-width of the diffraction peak of the anatase TiO$_2$ (1 0 1) plane. Figure 3 shows the relationship between the crystallite size of the obtained anatase TiO$_2$ particles and the concentration of the OH groups derived from the polyol and sugar alcohol molecules in the aqueous solution. The used polyols and sugar alcohols are ethylene glycol, glycerin, meso-erythritol, and D-mannitol, which have two, three, four, and six OH groups per molecule, respectively. The crystallite size decreased from ca. 6.5 nm to ca. 4.0 nm with increases in the concentration of OH groups in the aqueous solution. Furthermore, in the case that the aqueous solution of ethylene glycol, glycerin, and meso-erythritol was used for the hydrolysis reaction, a decrease in the crystallite size of the obtained anatase TiO$_2$ particles occurred when the concentration of the OH groups in the aqueous solution was larger than c.a. 0.5 mol/l. On the other hand, in the case that the D-mannitol aqueous solution was used, a decrease in the crystallite size occurred when the concentration of the OH groups in the solution was larger than 0.01 mol/l. Thus, in the case that the D-mannitol, which is a hexanol and one of sugar alcohol molecules, was used for the hydrolysis reaction of TIP, the degree of crystallization of the obtained TiO$_2$ particles was greatly affected compared with the other diol, triol, and tetraol (meso-erythritol) molecules that were used. This phenomenon indicates that D-mannitol has the ability to inhibit the crystallization of TiO$_2$ during the hydrolysis reaction by heating the mixture of TIP and the D-mannitol aqueous solution due to the interaction between Ti$^{4+}$ ions and the OH groups in the D-mannitol molecules. The strength of the effects of polyols and sugar alcohols on the crystallization of the TiO$_2$ particles also greatly depended on the number of OH groups in the polyol molecules. In general, the number of OH groups in a sugar alcohol molecule is more than four. Sugar alcohols are therefore useful agents for regulating the hydrolysis reaction.

3.2 Formation of TiO$_2$–sugar alcohol complexes and their characterization

In the previous section, the particles obtained by the hydrolysis reaction of TIP with a polyol or a sugar alcohol aqueous solution were characterized. We next examined the interaction between the sugar alcohol molecules and the TiO$_2$ particles in the obtained particles. Figure 4 shows that the relation between the molar ratio of organic molecule/Ti in the obtained particles and the concentrations of the used polyol or the sugar alcohol aqueous solution. The organic molecules in
the obtained particles are the polyl or sugar alcohol molecules which dissolved in the aqueous solution used for the hydrolysis reaction. The amount of organic molecules was estimated from the results of the CHN element analysis. When the ethylene glycol aqueous solution was used for the hydrolysis reaction, the organic molecule/Ti molar ratio was around 0.08. When the glycerin aqueous solution was used for the hydrolysis reaction, the organic molecule/Ti molar ratio increased from 0.05 to 0.16, with a concentration range from 0.1 mol/l to 1 mol/l. In the case that the meso-erythritol aqueous solution was used for the hydrolysis reaction, the organic molecule/Ti molar ratio increased from 0.07 to 0.27 with a concentration range from 0.05 mol/l to 1 mol/l. Furthermore, in the case that D-mannitol aqueous solution was used for the hydrolysis reaction, the organic molecules/Ti molar ratio began to increase at 0.005 mol/l of the D-mannitol aqueous solution. In the case that D-mannitol aqueous solution was used for the hydrolysis reaction, the concentration at which the organic molecule/Ti molar ratio began to increase was quite less than that of other sugar alcohol and polyol molecules. If pure TiO₂ particles were formed, the organic molecule/Ti molar ratio will be 0. However, the organic molecule/Ti molar ratio was not 0. These results shown in Fig. 4 indicate that the obtained powder was a complex between TiO₂ and organic molecules. Furthermore, it is considered that the interaction between Ti⁺ ions and polyl or sugar alcohol molecules strongly depends on the number of OH groups per a molecule, since the coordination of OH groups in the molecules is the dominant interaction between them. The complex formation between TiO₂ and organic molecules was affected by the chelate effect.

**Figure 5** shows the DTA curves of the complex powder prepared by heating the mixture of TIP and the polyl or the sugar alcohol aqueous solution at 368 K for 24 h. In the case that ethylene glycol was used for preparing the complex, strong exothermic and endothermic peaks were not observed in the DTA curve of the complex powder, as shown in Fig. 5 (a). This result indicates that the obtained powder contained only low levels of organic compounds. This result agrees with the result shown in Fig. 4. When glycerin was used for the hydrolysis reaction, an exothermic peak was observed around 550 K, as shown in Fig. 5 (b). This peak corresponds to the oxidation of organic compounds such as glycerin and the unreacted TIP in the complex powder. Figure 5 (c) shows the DTA curve of the complex powder prepared by heating the mixture of TIP and meso-erythritol aqueous solution. The meso-erythritol has four OH groups per a molecule and is a sugar alcohol. The exothermic peak, which can be assigned to the oxidation of organic compounds in the complex powder, was also observed around 550 K. Furthermore, a shoulder peak at around 650 K was observed. In the TG curve, no weight loss was observed around this temperature range. This peak therefore corresponds to the crystallization of the amorphous TiO₂ to anatase phase. Figure 5 (d) shows the DTA curve of the complex powder prepared by heating the mixture of TIP and D-mannitol aqueous solution. The exothermic peaks, which correspond to the oxidation of organic compounds in the complex powder and the crystallization, were also observed around 550 K and 750 K, respectively. Furthermore, another exothermic peak around 850 K was observed. This peak corresponds to the oxidation of the D-mannitol molecules, which strongly coordinated to the Ti⁺ ions. Weight loss around 850 K was also observed in the TG curve of the complex powder. In the case that the interaction between Ti⁺ ions and the polyl or the sugar alcohol molec-

![Fig. 4](image-url)  
**Fig. 4.** Relation between the concentration of the polyl and the sugar alcohol aqueous solution and the organic molecule/Ti molar ratio in the particles prepared by heating the mixture of TIP and the polyl or sugar alcohol aqueous solution. The polyol and sugar alcohol molecules used for heating with TIP: (○) ethylene glycol, (■) glycerin, (□) meso-erythritol, and (●) D-mannitol.

![Fig. 5](image-url)  
**Fig. 5.** DTA curves of the complex powders prepared by heating the mixture of TIP and 0.5 mol/l of polyl or sugar alcohol aqueous solution at 368 K for 24 h. The polyl and sugar alcohol molecules used for heating with TIP: (a) ethylene glycol, (b) glycerin, (c) meso-erythritol, and (d) D-mannitol.
where the heating with TIP, the concentrations of Ti solution of meso-erythritol and D-mannitol was used for heating at 368 K for 24 h. The polyol and sugar alcohol molecules used for heating with TIP: \( \square \) meso-erythritol, and \( \bullet \) D-mannitl.

According to the result shown in Fig. 6, when the aqueous solutions of meso-erythritol and D-mannitol were used for heating with TIP, the number of sugar alcohol molecules coordinated by the sugar alcohol molecules was proportional to the aqueous solution used for heating with TIP at 368 K for 24 h. When the aqueous solutions of meso-erythritol and D-mannitol were used, the slopes of the fitted line were 1.13 and 2.00, respectively. The Ti ions in neutral aqueous solution are easily precipitated by the hydrolysis reaction of TIP, so that the degree of crystalization depended on the number of OH groups in the polyol or the sugar alcohol molecule.

In the case that a complex between Ti\( ^{4+} \) ions and the sugar alcohol molecules is formed, the complex will dissolve in water due to the OH groups in the sugar alcohol molecules. Figure 6 shows the relation between the concentration of the sugar alcohol in the aqueous solution used for heating with TIP and the concentrations of Ti\( ^{4+} \) ions in the aqueous solution after heating at 368 K for 24 h. When the aqueous solutions of meso-erythritol and D-mannitol were used for heating with TIP, a linear relationship was observed between the logarithm of the concentration of sugar alcohol and the logarithm of the concentration of Ti\( ^{4+} \) ions in the solution. The line fitting was carried out by the least square method. In the case that meso-erythritol and D-mannitol were used, the slopes of the fitted line were 1.13 and 2.00, respectively. The Ti\( ^{4+} \) ions in neutral aqueous solution are easily precipitated by the hydrolysis reaction. Thereby, the concentrations of Ti\( ^{4+} \) ions in the aqueous solution are equal to those of the Ti\( ^{4+} \) ions coordinated by the sugar alcohol molecules (\([\text{Ti}^{4+}-\text{sugar alcohol}]\)). According to the result shown in Fig. 6, when the aqueous solution of meso-erythritol and D-mannitol was used for heating with TIP, the concentrations of Ti\( ^{4+} \) ions coordinated by the sugar alcohol molecules were proportional to the [meso-erythritol]\( ^{13} \) and [D-mannitol]\( ^{20} \), respectively. Here, [meso-erythritol] and [D-mannitol] are the concentrations of the meso-erythritol and D-mannitol aqueous solutions, respectively. The stability coefficient (\( K \)) of the complex between Ti\( ^{4+} \) ion and the sugar alcohol molecules can be described as follows:

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K = [\text{Ti}^{4+}-\text{sugar alcohol}] / ([\text{Ti}^{4+}] \cdot [\text{sugar alcohol}]^n),
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where \( n \) is the number of sugar alcohol molecules coordinated to the Ti\( ^{4+} \) ion. Accordingly, the number of sugar alcohol molecules in the complex can be estimated by the value of \( n \). Therefore, when meso-erythritol and D-mannitol were used for heating with TIP, the number of sugar alcohol molecules which coordinated to the Ti\( ^{4+} \) ion was \( n = 1 \) and \( n = 2 \), respectively. This result agrees with the fact that the strength of the coordination of D-mannitol molecules to Ti\( ^{4+} \) ion is stronger than that of meso-erythritol. The formation of the complex between a Ti\( ^{4+} \) ion and sugar alcohol molecules affected the hydrolysis reaction of TIP, so that the degree of crystallization depended on the number of OH groups per a sugar alcohol molecules used.

### 3.3 Synthesis of TiO\(_2\)-D-mannitol complex nanoparticles and their photocatalytic activity

Morphology of the TiO\(_2\)-sugar alcohol complex prepared by heating of TIP in a sugar alcohol aqueous solution was an aggregated precipitate. In order to characterize the photocatalytic activity and other properties of the complex, the stable sol with the homogeneous dispersion of TiO\(_2\)-sugar alcohol complex nanoparticles is preferred. The preparation of TiO\(_2\)-sugar alcohol complex nanoparticles was examined by heating of the TiO\(_2\)-D-mannitol complex in 0.5 mol/L HNO\(_3\) aqueous solution for 24 h. It is expected that the removal of excess D-mannitol molecules from the TiO\(_2\)-D-mannitol complex precipitate will form the TiO\(_2\)-D-mannitol complex nanoparticles. Furthermore, sugar alcohol molecules are hydrophilic so that a small amount of sugar alcohol molecules in the complex enables to form the stable dispersion of the TiO\(_2\)-sugar alcohol complex nanoparticles in an aqueous solution. The homogenous dispersion contributes to improve the efficiency of the photocatalytic activity.

Figure 7 shows the XRD patterns of the powder obtained by heating 0.5 g of the TiO\(_2\)-D-mannitol complex in 100 ml of the 0.5 mol/L HNO\(_3\) aqueous solution for 24 h. According to the XRD pattern shown in Fig. 7(a), the TiO\(_2\)-D-mannitol complex used for the heat treatment was amorphous. When the heating temperature in the HNO\(_3\) aqueous solution were 318 K, 328 K, 348 K, and 368 K, the XRD patterns of the

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**Fig. 6.** Relation between the concentration of Ti\( ^{4+} \) ion in the aqueous solution and the concentration of the sugar alcohol aqueous solution used for heating with TIP at 368 K for 24 h. The polyol and sugar alcohol molecules used for heating with TIP: \( \square \) meso-erythritol, and \( \bullet \) D-mannitol.

**Fig. 7.** XRD patterns of the obtained TiO\(_2\)-D-mannitol complex nanoparticles prepared by heating the TiO\(_2\)-D-mannitol complex in HNO\(_3\) aqueous solution for 24 h. The heating temperatures were: (a) without heat treatment, (b) 318 K, (c) 328 K, (d) 348 K, and (e) 368 K.
obtained particles were shown in Figs. 7(b), (c), (d), and (e), respectively. These patterns can be assigned to anatase TiO$_2$. Accordingly, the low temperature heat treatment of the TiO$_2$–D-mannitol complex in HNO$_3$ at 318 K for 24 h formed crystallized anatase TiO$_2$ particles. Furthermore, the FWHM of the XRD peaks decreased with an increase of the heating temperature from 318 K to 368 K. This result indicated that the degree of crystallization of the obtained anatase particles increased at the higher heating temperature.

The open circles in Fig. 8 show the relation between the heating temperature and the C/Ti atomic ratio of the obtained complex particles. The C/Ti atomic ratio of the obtained complex particles decreased from 0.52 to 0.19 with an increase of the heating temperature. The carbon atoms in the obtained anatase particles originated from D-mannitol molecules. Accordingly, the obtained anatase was TiO$_2$–D-mannitol complex particles and the decrease of the C/Ti atomic ratio means that the hydrolysis reaction and dissolution-precipitation process of the complex was accelerated at higher heating temperature.

The closed circles in the Fig. 8 show the relation between the BET specific surface area (SBET) of the obtained complex particles and the heating temperature of the complex in the HNO$_3$ aqueous solution. The SBET decreased from 410 m$^2$/g to 310 m$^2$/g when the heating temperature in the HNO$_3$ aqueous solution increased from 318 K to 368 K. It is considered that the result indicates that the higher heating temperature accelerated the hydrolysis reaction so that the obtained particle size and porosity changed. The correlation between the C/Ti atomic ratio and the SBET also indicates that the dissolution-precipitation process of the TiO$_2$–D-mannitol complex occurred during the heating process of the complex in the HNO$_3$ aqueous solution.

**Figure 9** shows the FE-SEM images of the obtained TiO$_2$–D-mannitol complex particles by heating of the TiO$_2$–D-mannitol complex in 0.5 mol/l HNO$_3$ aqueous solution for 24 h. The heating temperatures were: (a) 318 K, (b) 328 K, (c) 348 K, and (d) 368 K.

The D-mannitol complex was heated in the HNO$_3$ aqueous solution at 318 K, 328 K, 348 K, and 368 K for 24 h, the average particle diameters of the obtained complex particles were 10 nm, 15 nm, 22 nm, and 55 nm, respectively. The particle diameter of the obtained complex nanoparticles increased with an increase of the heating temperature. In general, in the case that the heating temperature of the TiO$_2$–D-mannitol complex in HNO$_3$ aqueous solution increased, the hydrolysis reaction of the TiO$_2$–D-mannitol complex and the decomposition of the bond between a Ti$^{4+}$ ion and D-mannitol will be accelerated. It is considered that the above process would reduce the size of the obtained complex nanoparticles. However, the size of the obtained nanoparticles actually increased with an increase of the heating temperature. This result indicates that the formation process of the TiO$_2$–D-mannitol complex nanoparticles is consistent by not only the hydrolysis process but also dissolution-precipitation process. Furthermore, the decrease of the SBET with an increase of the heating temperature shown in Fig. 8 is consistent with the increase of the average particle diameter at higher heating temperature.

The D-mannitol molecules which exist on the surface of the complex nanoparticles greatly improve the stability of the TiO$_2$–D-mannitol complex nanoparticles in the aqueous solution. The dispersion of the TiO$_2$–D-mannitol complex nanoparticles kept the very stable dispersion in aqueous solution for more than a year. The homogenous dispersion contributes to improve the efficiency of the photocatalytic activity. The photocatalytic activity of anatase TiO$_2$ particles is very important characteristics. The TiO$_2$ particles in the TiO$_2$–D-mannitol complex nanoparticles have also anatase structure. Therefore, it is expected that the complex shows the photocatalytic activity. Furthermore, the large surface area of the complex nanoparticles as shown in Fig. 8 becomes an advantage as the photocatalyst. Then, the investigation of the photocatalytic activity of the TiO$_2$–D-mannitol complex nanoparticles is important.
bance peak position of methylene blue. The open circles in Fig. 10 shows the photocatalytic activity of the TiO$_2$–D-mannitol complex nanoparticles obtained by heating of the complex powder in the HNO$_3$ aqueous solution at 348 K. Although the complex nanoparticles prepared by heating at 348 K contain more amount of D-mannitol than those prepared at 368 K, the $I_{10}/I_{0}$ became less than 0.02 after the UV irradiation for 22 h. The closed circle in Fig. 10 shows the photocatalytic activity of the TiO$_2$–D-mannitol complex nanoparticles obtained by heating of the complex powder in the HNO$_3$ aqueous solution at 348 K. Although the complex nanoparticles prepared by heating at 348 K contain more amount of D-mannitol molecules than those prepared at 368 K, the $I_{10}/I_{0}$ became less than 0.02 after the UV irradiation for 15 h. The UV irradiation time to decompose the methylene blue molecule was less than that of the complex nanoparticles prepared at 368 K. Thus, the larger specific surface area contributed to the higher photocatalytic activity of the complex nanoparticles. Furthermore, the complex formation between TiO$_2$ and sugar alcohol molecules effectively improved the stability of the dispersion of the TiO$_2$ nanoparticles in H$_2$O. Thus, the D-mannitol molecules in the complex nanoparticles did not seriously hinder the photocatalytic activity. Furthermore, the obtained stable sol with the TiO$_2$–D-mannitol complex nanoparticles can be used for photocatalyst TiO$_2$ film preparation. The homogeneous dispersion of the TiO$_2$–D-mannitol complex nanoparticles contributed to improve the efficiency of the photocatalytic activity. The complex formation between TiO$_2$ and D-mannitol molecules can effectively control the characteristics of the TiO$_2$ nanoparticles.

4. Conclusion

Complexes between TiO$_2$ and sugar alcohol molecules or polyol molecules were prepared by heating the mixture of TIP and ethylene glycol, glycerin, meso-erythritol, or D-mannitol aqueous solution at 368 K for 24 h. The degree of crystallization of TiO$_2$ in the obtained TiO$_2$–sugar alcohol or polyol complex depended on the concentration of the polyol and sugar alcohol aqueous solution. When the TiO$_2$–sugar alcohol or polyol complex was prepared using the same concentration of the sugar alcohol or polyol aqueous solution, the degree of crystallization of the TiO$_2$ in the complex decreased with increase in the number of OH groups per molecule. The interaction between D-mannitol molecules and Ti$^{4+}$ ion greatly affected the crystallization process of TiO$_2$ in the complex. According to the results of the DTA measurements and the element analysis, the strength of the interaction between Ti$^{4+}$ ions and polyol or sugar alcohol molecules increased with increases in the number of OH groups in the molecules. The heat treatment of TiO$_2$–D-mannitol complex in 0.5 mol/l HNO$_3$ aqueous solution enabled us to obtain TiO$_2$–D-mannitol complex nanoparticles whose diameter was in the range from 10 nm to 55 nm. The dissolution-precipitation process of the complex played an important role for the formation of the complex nanoparticles. The high specific surface area and the homogeneous dispersion of the TiO$_2$–D-mannitol complex nanoparticles contributed to improve the efficiency of the photocatalytic activity.

References