

Research Article

Characterization of Titanium Oxide Nanoparticles Obtained by Hydrolysis Reaction of Ethylene Glycol Solution of Alkoxide

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Transparent and stable sols of titanium oxide nanoparticles were obtained by heating a mixture of ethylene glycol solution of titanium tetraisopropoxide (TIP) and a NH_3 aqueous solution at 368 K for 24 h. The concentration of NH_3 aqueous solution affected the structure of the obtained titanium oxide nanoparticles. For NH_3 aqueous solution concentrations higher than 0.2 mol/L, a mixture of anatase TiO_2 nanoparticles and layered titanate nanoparticles was obtained. The obtained sol was very stable without formation of aggregated precipitates and gels. Coordination of ethylene glycol to Ti^{4+} ions inhibited the rapid hydrolysis reaction and aggregation of the obtained nanoparticles. The obtained titanium oxide nanoparticles had a large specific surface area: larger than 350 m^2/g . The obtained titanium oxide nanoparticles showed an enhanced adsorption towards the cationic dye molecules. The selective adsorption corresponded to presence of layered titanate on the obtained anatase TiO_2 nanoparticles.

1. Introduction

Titanium dioxide (TiO_2 titania) is an n-type oxide semiconductor that shows photocatalytic activity and photoconductivity [1, 2]. Several various applications of TiO_2 particles have been studied in recent years, as photocatalysts and to solar cells, UV-shielding materials and electric devices [3–6]. For these applications, development of a simple synthesis method to obtain TiO_2 nanoparticles with highly homogeneous dispersion has been required [7, 8]. TiO_2 nanoparticles are also useful in many important applications for improving environmental problems [9, 10]. These nanoparticles can be used for formation of TiO_2 thin films with optical transparency and photocatalyst activity. Furthermore, surface characteristics of TiO_2 nanoparticles strongly affect the application area of TiO_2 nanoparticles. For example, Grätzel developed photoelectrochemical systems with dye-sensitized anatase TiO_2 semiconductor electrodes [11, 12]. The characteristics of these solar cells depend on adsorption interaction between dye molecules and TiO_2 nanoparticle surface. Therefore, it is also important to control molecular adsorption properties of TiO_2 nanoparticles.

Rath et al. prepared size-controlled TiO_2 nanoparticles in reverse micelles using a surfactant Aerosol-OT (AOT) [13]. Zaki et al. obtained anatase TiO_2 nanoparticles through hydrolysis of ethanol solution of titanium tetraisopropoxide by adding nitric acid [14]. They examined an adsorption of amine molecules to investigate the surface adsorption sites. Nakayama and Hyashi prepared stable sols of TiO_2 with surface modification of carboxylic acid and amine [15]. Some reports have also described methods for preparation of TiO_2 nanoparticles and stable sols using peroxotitanic acid as a precursor [16].

This study describes examination of a novel preparation method of titanium oxide nanoparticles and their stable sols through hydrolysis reaction of an ethylene glycol solution of titanium alkoxide with NH_3 aqueous solution. Ethylene glycol easily coordinates to Ti^{4+} ions and controls the hydrolysis reaction [17, 18]. Furthermore, NH_3 molecules also strongly coordinate to the Ti^{4+} ions. It is expected that restricting rapid hydrolysis reaction enables the production of titanium oxide nanoparticles without aggregation. Furthermore, surface characteristics of the titanium oxide nanoparticles were examined by measuring adsorption isotherms of cationic and anionic dye molecules.

2. Experiments

2.1. Preparation of Titanium Oxide Nanoparticles and Their Sols. The titanium oxide nanoparticles were prepared as follows. The 1 mol/L of NH_3 aqueous solution was added to the 50 mL of ethylene glycol solution (0.1 mol/L) of titanium tetraisopropoxide (TIP). The total volume was adjusted to 100 mL. Under these circumstances no precipitate was observed, although an opaque solution was obtained. This solution was heated at 368 K for 24 h in a closed glass vessel, and a stable sol was obtained without precipitation. All chemicals used in this preparation were of reagent grade (Wako Pure Chemical Industries Ltd.). To control the particle size and surface properties of the obtained titanium oxide nanoparticles, the same synthetic process was also conducted using the NH_3 (aq) with other concentrations. The concentrations were in the range of 0.1 mol/L–1 mol/L. Hereinafter, this concentration will be designated as $[\text{NH}_3]$.

To separate the obtained particles from the sol, 50 mL of the obtained sol was poured into a cellulose tube for dialysis, and the cellulose tube was soaked in 500 mL of H_2O for 3 h at room temperature. The 500 mL of H_2O was exchanged five times. Finally, the sol in the cellulose tube was dried at 348 K for 12 h.

Anatase TiO_2 particles were also prepared using a simple hydrolysis reaction between Ti alkoxide and H_2O . The H_2O was added to 0.01 mol of TIP. Then the total volume was adjusted to 100 mL. The mixed solution of TIP and H_2O was kept in a closed glass beaker and heated at 368 K for 24 h. White precipitate was obtained using the hydrolysis reaction. The precipitate was separated by centrifugation at 3000 rpm for 5 min. The obtained precipitate was dried at 348 K for 24 h.

2.2. Characterization. The structure of the obtained particles was characterized using X-ray diffraction (XRD) (Cu $K\alpha$ 40 kV, 100 mA, MXP-18; Bruker AXS Co., Ltd.). The particle shape was observed using field emission scanning electron microscopy (FE-SEM; JSM-6330; JEOL) after osmium coating, which is one of the electroconductive film formation methods for electron microscope observation. It is the method for depositing osmium metal thin film on the sample surface by DC glow discharge in osmium oxide gas. The ultraviolet-visible (UV-VIS) spectra of the sols and the solutions were measured using quartz cell (UV2000; Hitachi Ltd.) with wavelengths of 300–800 nm, and the optical path length of the cell was 1 cm. Thermogravimetric analysis and differential thermal analysis (TG-DTA) were measured in the air with the flow rate = 100 mL/min. Weight of the used samples was 10 mg, and the rate of elevating temperature was 10 K/min. The upper limit of the measuring temperature was 1073 K. The N_2 adsorption isotherms of the obtained powders were measured at 77 K by using the volumetric method (BELSORP-max, BEL Japan, Inc.) after pretreatment at 383 K in 1 mPa for 1 h. The used sample weight was ca. 0.1 g.

2.3. Dye Adsorption Measurement. Dye adsorption isotherms of the titanium oxide nanoparticles were measured as

described below. First, 50 mL of methylene blue aqueous solutions was prepared and adjusted to the following concentrations: 1×10^{-4} mol/L, 2×10^{-4} mol/L, 3×10^{-4} mol/L, 4×10^{-4} mol/L, 6×10^{-4} mol/L, and 8×10^{-4} mol/L. 0.05 g of the titanium oxide powder was added to 50 mL of each of the methylene blue aqueous solution. The pH values of the dye aqueous solution with dispersion of the titanium oxide powder were in the range from 6.5 to 7.5 before and after the adsorption. Each dye aqueous solution with the titanium oxide powder was stirred at 500 rpm at 298 K for 24 h to reach the equilibrium of dye adsorption. From each solution, 3 mL of the methylene blue aqueous solution was separated using filtration with a $0.45 \mu\text{m}$ membrane filter. The optical absorbance of the corrected methylene blue aqueous solution at 655 nm was measured using a UV-VIS spectrometer (UV2000; Hitachi Ltd.). The methylene blue concentrations were calculated from the absorbance using a working curve. Measurements of the dye adsorption isotherm described above were also conducted using other dyes such as crystal violet, Evans blue, and eosin Y. The respective wavelengths used for estimating the dye aqueous solution concentrations of crystal violet, Evans blue, and eosin Y were 590 nm, 608 nm, and 517 nm.

3. Results and Discussion

3.1. Characterization of the Obtained Titanium Oxide Nanoparticles. Figure 1 portrays XRD patterns of the particles obtained by heating the mixture of ethylene glycol solution of TIP and NH_3 (aq) at 368 K for 24 h. The XRD peaks in Figures 1(a)–1(e), as marked with open circles, can be assigned to anatase TiO_2 . When the concentration of the NH_3 (aq) concentration mixed with the ethylene glycol solution of TIP was 0.1 mol/L, the obtained titanium oxide was anatase TiO_2 as shown in Figure 1(a). When the mixture of TIP and H_2O was heated at 368 K for 24 h, anatase TiO_2 was also obtained as shown in Figure 1(e). In Figure 1(b), a very weak and broad peak around $2\theta < 10^\circ$ can be assigned to layered titanate structure [19]. When the NH_3 (aq) concentration became higher than 0.2 mol/L, the XRD peaks shown in Figures 1(b)–1(d) can be assigned to layered titanate lattice and anatase TiO_2 . Accordingly, the NH_3 (aq) concentration affected the crystal structure of the obtained particles. Furthermore, crystallite sizes were determined by using Scherrer's equation at the peak of anatase TiO_2 (101) plane at $2\theta = 25.8^\circ$. The crystallite sizes determined from the XRD patterns of Figures 1(a)–1(e) were 4.68 nm, 4.60 nm, 2.88 nm, 2.27 nm, and 10.7 nm, respectively. Accordingly, a decrease in crystallite size was observed with increases in the NH_3 (aq) concentration. Furthermore, the crystallite size of anatase TiO_2 of Figure 1(a) was smaller than that of Figure 1(e). This result means that growth of the crystallite size of the anatase TiO_2 particles was restricted by coordination of the coexisted NH_3 and ethylene glycol molecules in the solution.

Figure 2 shows FE-SEM images of the obtained titanium oxide particles. Figures 2(a), 2(b), and 2(c), respectively, show FE-SEM images of particles obtained using the NH_3

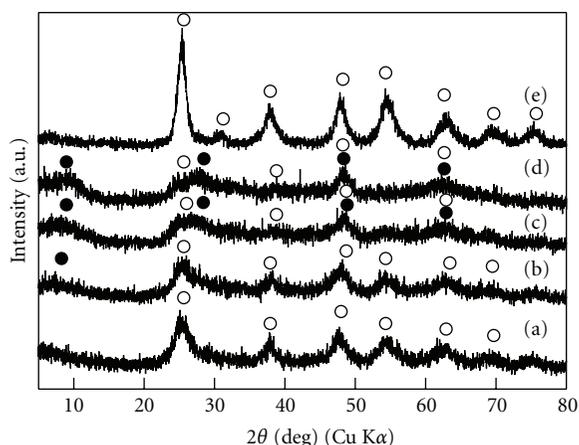


FIGURE 1: XRD patterns of the obtained particles by heating a mixture of ethylene glycol solution of TIP and NH_3 (aq) at 368 K for 24 h. The NH_3 (aq) concentrations were (a) 0.1 mol/L, (b) 0.2 mol/L, (c) 0.5 mol/L, (d) 1 mol/L, and (e) the particles obtained by heating the mixture of TIP and H_2O at 368 K for 24 h. ○: anatase TiO_2 and ●: layered titanate.

(aq) at concentrations of 0.1 mol/L, 0.5 mol/L, and 1 mol/L. When the $[\text{NH}_3]$ values were 0.1 mol/L, 0.5 mol/L, and 1 mol/L, the average particle sizes were 32.1 nm, 31.5 nm, and 28.0 nm, respectively. The particle sizes of the obtained titanium oxide particles were almost close to each other. The coordination of NH_3 aqueous solution did not affect the particle size of the titanium oxide nanoparticles, although as discussed in Figure 1, the crystal structure was affected. The average particle sizes determined by FE-SEM images of the titanium oxide nanoparticles were larger than the crystallite sizes determined by using Scherrer's equation. This means that the particles observed in the FE-SEM images had aggregated structure of crystallites. Furthermore, when the NH_3 (aq) concentration was more than 0.5 mol/L, the particle shape would change from spherical particles to plate particles. This will be one of the reasons of difference between the crystallite size and the average particle size.

To examine the residual organic molecules and the degree of the crystallization of the obtained nanoparticles, the TG-DTA curves were measured. Figure 3(a) shows the TG-DTA curve of the nanoparticles obtained by using the NH_3 (aq) ($[\text{NH}_3] = 0.1$ mol/L). The TG curve had 15.1% weight loss below 400 K. This weight loss corresponded to desorption of adsorbed H_2O on the nanoparticles. Furthermore, when the temperature was around 523 K, a steep decrease of weight was observed. According to the DTA curve, a sharp exothermic peak also appeared around 523 K. Therefore, the weight loss around 523 K corresponded to the oxidation of the TIP molecules which did not react in the hydrolysis reaction. The weight loss around this temperature was 8.1%. Furthermore, a slight decrease of weight (4.82%) occurred at temperatures of 530 K to 700 K. This weight loss corresponded to dehydration of surface OH groups and desorption of the adsorbed ammonium ions. Figure 3(b) shows the TG-DTA curve of the nanoparticles obtained using the NH_3 (aq) ($[\text{NH}_3] = 1$ mol/L). In this case, 24% of the

large weight loss caused by desorption of adsorbed H_2O was also observed below 400 K. The DTA curve had an exothermic peak around 535 K, and the temperature was close to that of Figure 4(a). Therefore, this DTA peak corresponds to the oxidation of organic molecules. The weight loss around this temperature was 2.4%. This value of the weight loss in Figure 3(b) was less than that in Figure 3(a). This result means that TIP molecules in the 1 mol/L of NH_3 (aq) are more effectively hydrolyzed than those in the 1 mol/L of NH_3 (aq). Furthermore, the slight decrease in mass corresponded to desorption of ammonium ions and the surface OH groups, as discussed in Figure 3(a). Accordingly, the hydrolysis reaction of titanium alkoxides proceeded more effectively at higher concentrations of NH_3 (aq).

3.2. Investigation of Dispersion Stability and Formation Process of Sols by Using UV-VIS Absorption Spectra Measurements.

To examine dispersed state of particles in the obtained sols, UV-VIS absorption spectra were measured as presented in Figure 4. When the $[\text{NH}_3]$ was 0.05 mol/L, the value of optical absorbance at 400 nm was 0.35. In this case, the obtained solution was a slightly opaque sol. Then, the observed optical absorbance corresponded to scattering of light. Furthermore, when wavelength decreased from 400 nm to 320 nm, the optical absorbance increased from 0.35 to 3.00. This increase of the optical absorbance corresponds to the electron transition between band gap of TiO_2 . In general, a charge transfer transition between O^{2-} ion and Ti^{4+} ion also causes optical absorption in this wavelength range [20]. Figures 4(f)–4(h) show optical absorption spectra of isopropanol solution of TIP whose concentrations were, respectively, 1 mol/L, 0.1 mol/L, and 0.01 mol/L. According to Figure 4(f), the absorption edge of the charge transfer transition was around 355 nm when the concentration of the isopropanol solution of TIP was 1 mol/L. As shown in Figures 4(f)–4(h), with decreasing the TIP concentration in the solution from 1 mol/L to 0.01 mol/L, the wavelength of the absorption edge shifted from 355 nm to a shorter wavelength. Because the maximum concentration of TIP in the obtained sol was 0.05 mol/L, the absorption edge, which corresponded to the charge transfer, was expected to be less than 355 nm. The strong absorption around 375 nm in Figure 4(a) accordingly corresponded to the band gap transition of electrons in TiO_2 . When the $[\text{NH}_3]$ were greater than 0.1 mol/L, the optical absorbance at 400 nm was less than 0.05. Therefore, the obtained sol was almost transparent for visible light, and the scattering of light by the particles in the sol was slight. Therefore, transparent and homogeneous sols without precipitate are obtainable merely by heating the mixture of ethylene glycol solution of TIP and NH_3 (aq). Furthermore, the wavelength of the absorption edge decreased with the increase of the $[\text{NH}_3]$, and the wavelengths remained longer than 360 nm. The strong optical absorption corresponded to the band gap electron transition of TiO_2 and indicated the formation of TiO_2 particles in the solution during the heating process.

To examine the formation process of titanium oxide nanoparticles in the TIP solution, we examined change

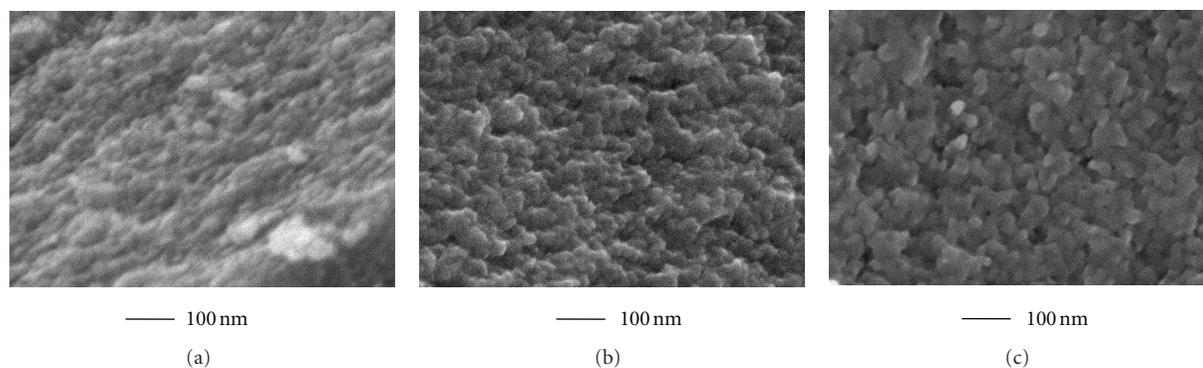


FIGURE 2: FE-SEM images of the titanium oxide particles obtained by heating the mixture of ethylene glycol solution of TIP and NH_3 (aq) at 368 K for 24 h. The $[\text{NH}_3]$ values were (a) 0.1 mol/L, (b) 0.5 mol/L, and (c) 1 mol/L.

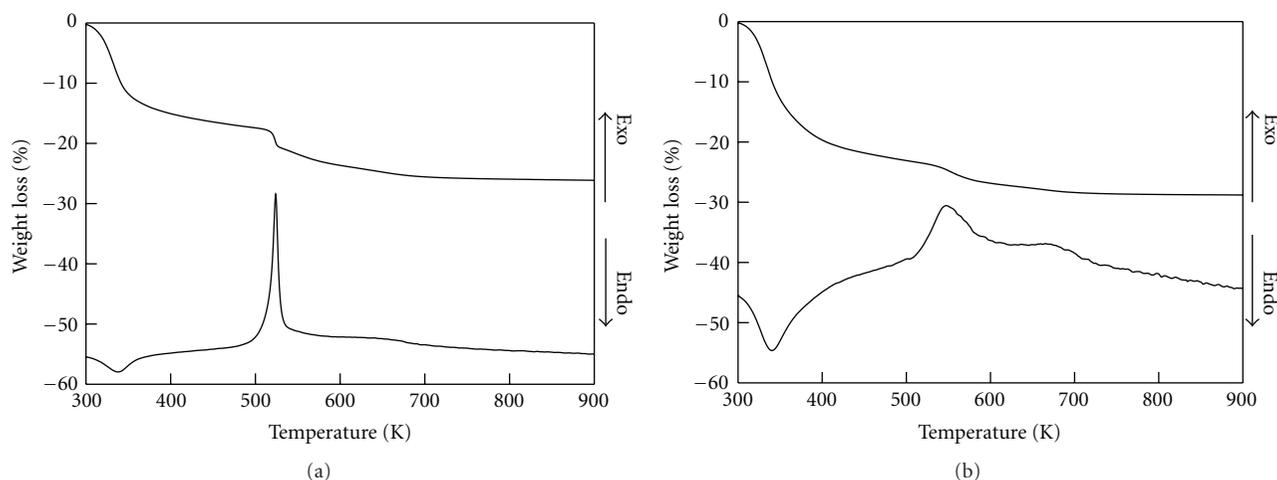


FIGURE 3: TG-DTA curves of the titanium oxide nanoparticles obtained by heating the mixture of ethylene glycol solution of TIP and NH_3 (aq). The $[\text{NH}_3]$ values were (a) 0.1 mol/L and (b) 1 mol/L.

of UV-VIS absorption spectra of the solution during the heating process. Figure 5 portrays the UV-VIS absorption spectra of the sols obtained by heating the mixture of ethylene glycol solution of TIP and NH_3 (aq) at 368 K. As presented in Figure 5(a), when the heating time was 0 h, that is, before the heat treatment, value of the optical absorbance at 400 nm was 0.52. The obtained solution was an opaque sol. Then, the observed optical absorbance corresponded to scattering of light. The optical absorbance increased from 0.35 to 3.00 for wavelengths of 400–320 nm. This spectrum resembled that portrayed in Figure 2(g). Therefore, this increase of the optical absorbance corresponds to the charge transfer transition between O^{2-} ion and Ti^{4+} ion. As presented in Figure 5(b), the optical absorbance at 400 nm of the solution that had been heated for 1 h was 0.01. Accordingly, the obtained solution was almost transparent in the visible light wavelength range. The absorption edge was 344 nm. When heating times were longer than 1 h, the optical absorption at 400 nm remained almost 0, which indicates that the solution was transparent and the clear sol was obtained. The absorption edge of the steep increase of absorbance shifted from 344 nm to 359 nm when the heating

time increased from 0 h to 24 h. This shift of the wavelength of the absorption edge indicated the formation of anatase TiO_2 lattice. If the shift of the adsorption edge was caused by decrease of the concentration of TIP in the solution, the wavelength of the charge transfer absorption would shift to shorter wavelength with increase of the heating time. The band gap energy, which corresponds to the wavelength of the absorption edge, depends on the size of nanoparticles by the quantum size effect. Therefore, the shift of the absorption edge signifies formation of titanium oxide and change of its particle sizes. Accordingly, the heating of the mixture of ethylene glycol solution of TIP and NH_3 (aq) at 368 K for more than 1 h was sufficient to obtain the transparent and homogeneous sol of titanium oxide nanoparticles.

3.3. Dye Adsorption Characteristics of the Titanium Oxide Nanoparticles Obtained by Hydrolysis Reaction of Ethylene Glycol Solution of TIP. To examine the surface properties of the obtained titanium oxide nanoparticles, the N_2 adsorption isotherms at 77 K were measured, and the BET-specific surface area was estimated. Figure 6 shows N_2 adsorption isotherms of the titanium oxide nanoparticles obtained with

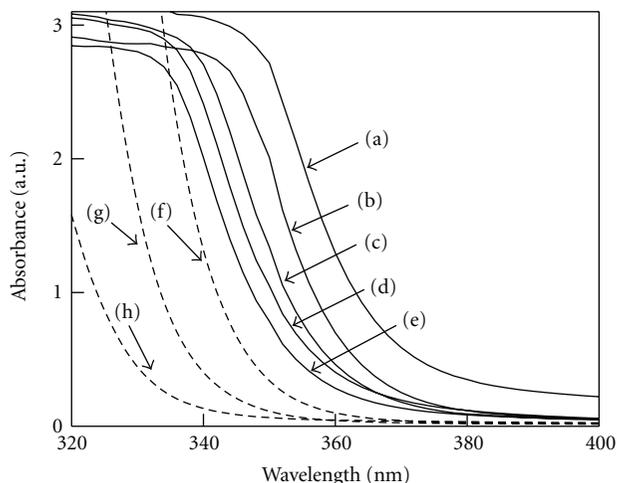


FIGURE 4: UV-VIS absorption spectra of the sols obtained by heating the mixture of ethylene glycol solution of TIP and NH_3 (aq) at 368 K for 24 h. The solid line shows the spectra of the obtained sols. The NH_3 (aq) concentrations were (a) 0.05 mol/L, (b) 0.1 mol/L, (c) 0.2 mol/L, (d) 0.5 mol/L, and (e) 1 mol/L. The broken lines show spectra of the isopropanol solution of TIP. The TIP concentrations of the solutions were (f) 1 mol/L, (g) 0.1 mol/L, and (h) 0.01 mol/L.

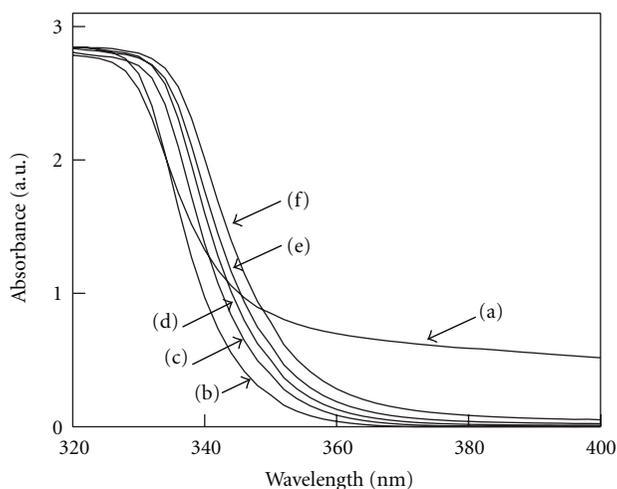


FIGURE 5: UV-VIS absorption spectra of the mixture of ethylene glycol solution of TIP and NH_3 (aq) ($[\text{NH}_3]=1$ mol/L). The heating temperature was 368 K. The heating times were the following: (a) 0 h (before heating), (b) 1 h, (c) 3 h, (d) 6 h, (e) 12 h, and (f) 24 h.

0.1 mol/L and 1 mol/L of the NH_3 (aq). Additionally, a N_2 adsorption isotherm of the conventional anatase TiO_2 particles obtained by heating the mixture of TIP and H_2O at 368 K for 24 h is also shown in Figure 6. Both N_2 adsorption isotherms obtained with the NH_3 aqueous solutions belong to the type I isotherms defined by IUPAC. The N_2 adsorption isotherm of the conventional anatase TiO_2 particles belongs to the type IV isotherm, and the hysteresis loop can be classified to the type H2 [21]. The N_2 adsorption isotherms of the titanium oxide nanoparticles were analyzed by using BJH method to estimate the average pore sizes and the total

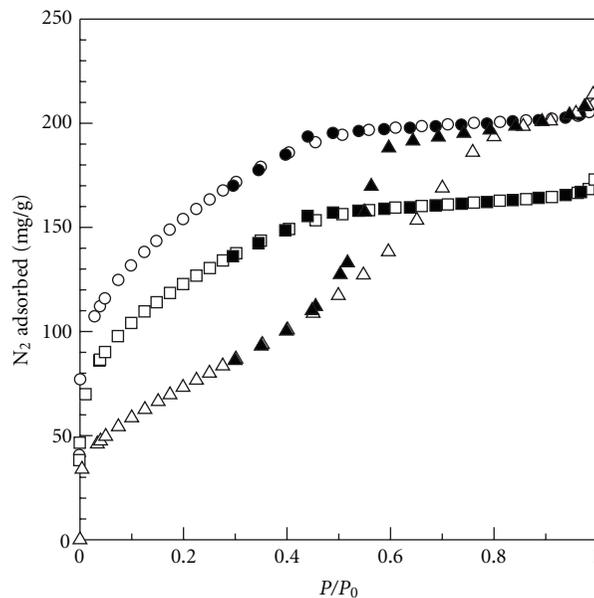


FIGURE 6: N_2 adsorption isotherms of the titanium oxide nanoparticles obtained by heating the mixture of ethylene glycol solution of TIP and NH_3 (aq) at 77 K. \circ , \bullet : adsorption and desorption isotherms of $[\text{NH}_3]=1$ mol/L. \square , \blacksquare : adsorption and desorption isotherms of $[\text{NH}_3] = 0.1$ mol/L. \triangle , \blacktriangle : adsorption and desorption isotherms of particles obtained by heating the mixture of TIP and H_2O at 368 K for 24 h.

pore volume. The N_2 adsorption isotherms were analyzed using the Brunauer-Emmett-Teller (BET) equation, allowing us to obtain the specific surface area of the titanium oxide nanoparticles (S_{BET}). The results of calculation were indicated in Table 1. When the $[\text{NH}_3]$ values were 0.1 mol/L and 1 mol/L, the S_{BET} values were, respectively, $358 \text{ m}^2/\text{g}$ and $445 \text{ m}^2/\text{g}$. With the higher concentration of NH_3 (aq), coordination of NH_3 molecules to Ti^{4+} ions inhibited rapid growth and aggregation of the nanoparticles so that higher specific surface area were achieved. However, the S_{BET} value of the anatase TiO_2 particles obtained by heating the mixture of TIP and H_2O was $214 \text{ m}^2/\text{g}$. Accordingly, the titanium oxide nanoparticles obtained using the reaction between the ethylene glycol solution of TIP and NH_3 (aq) had quite large S_{BET} values compared to those particles obtained using the conventional hydrolysis reaction of TIP. As, shown in the Table 1, the total pore volumes of the titanium oxide nanoparticles obtained with 0.1 mol/L and 1 mol/L of NH_3 aqueous solutions were $0.12 \text{ cm}^3/\text{g}$ and $0.13 \text{ cm}^3/\text{g}$, respectively, and they had very close values. The average pore sizes of the nanoparticles obtained with the 0.1 mol/L of NH_3 (aq) were larger than those obtained with the 1 mol/L of NH_3 (aq). Both of the average pore sizes were smaller than 2 nm so that the nanoparticles obtained with NH_3 (aq) were microporous materials. On the other hand, the average pore size of the anatase TiO_2 particles obtained by heating the mixture of TIP and H_2O was 4.67 nm. Accordingly, the obtained anatase TiO_2 was a mesoporous material. The dependence of the porosity and the pore size on the NH_3

TABLE 1: The BET specific surface areas of the nanoparticles obtained by heating the mixture of the ethylene glycol solution of TIP and the NH_3 aqueous solution. Average pore diameter and total pore volume were estimated by using the BJH method to the N_2 adsorption isotherms shown in Figure 6.

The solution added to ethyleneglycol solution of TIP	$[\text{NH}_3] = 0.1 \text{ M}$	$[\text{NH}_3] = 1 \text{ M}$	H_2O
S_{BET}	$358 \text{ m}^2/\text{g}$	$445 \text{ m}^2/\text{g}$	$214 \text{ m}^2/\text{g}$
Average pore diameter	1.34 nm	1.17 nm	4.67 nm
Total pore volume	$0.12 \text{ cm}^3/\text{g}$	$0.13 \text{ cm}^3/\text{g}$	$0.25 \text{ cm}^3/\text{g}$

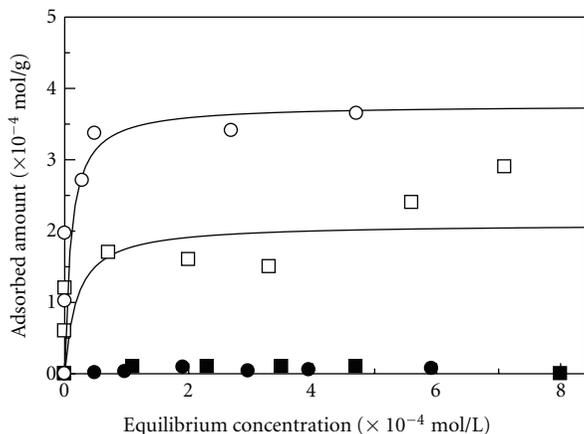


FIGURE 7: Adsorption isotherms of dye molecules on the titanium oxide nanoparticles in aqueous solution of dye. Aqueous solutions of the dye molecules were the following: \circ , methylene blue; \square , crystal violet; \bullet , Evans blue; \blacksquare , eosin Y. The titanium oxide nanoparticles were prepared using the aqueous solution having $[\text{NH}_3]$ of 1 mol/L.

(aq) concentration reflected the difference of the hydrolysis reaction in the solutions.

Adsorption isotherms of dye molecules were measured to investigate the interaction between the dye molecules and the titanium oxide nanoparticle surfaces. Figure 7 presents adsorption isotherms of dye molecules on the titanium oxide nanoparticles obtained at $[\text{NH}_3]=1 \text{ mol/L}$. The adsorption isotherms of the cationic dye molecules of methylene blue and crystal violet on the obtained titanium oxide nanoparticles are shown, respectively, as open circles and open squares. The black line shows the result of least-square curve-fitting based on Langmuir equation, which fits the experimental data very well. The saturated adsorbed amount of methylene blue and crystal violet was, respectively, $3.59 \times 10^{-4} \text{ mol/g}$ and $2.02 \times 10^{-4} \text{ mol/g}$. The adsorption isotherms of the anionic dye molecules of eosin Y and Evans blue on the titanium oxide nanoparticles are shown, respectively, as closed squares and closed circles. The saturated adsorbed amounts of eosin Y and Evans blue, as calculated from the Langmuir plots, were, respectively, $8.25 \times 10^{-6} \text{ mol/g}$ and $6.91 \times 10^{-6} \text{ mol/g}$. Accordingly, the saturated adsorbed amounts of the anionic dye molecules were less than 1/50 of those of the cationic dye molecules. Highly selective adsorption of the cationic dye molecules was observed.

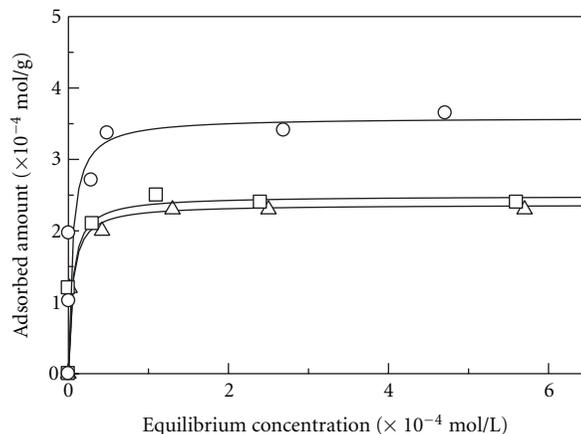


FIGURE 8: Adsorption isotherms of methylene blue on the titanium oxide nanoparticles in aqueous solution of dye. The NH_3 aqueous solutions concentrations used to prepare the titanium oxide nanoparticles were the following: \circ , 1 mol/L; \square , 0.2 mol/L; Δ , 0.1 mol/L.

To examine more details of the selective adsorption of the cationic dye molecules, the adsorption isotherms of methylene blue, which is a cationic dye molecule, were measured as presented in Figure 8. The adsorbents were titanium oxide nanoparticles prepared by using NH_3 (aq) whose concentrations were 0.1 mol/L, 0.2 mol/L, and 1 mol/L. The saturated adsorbed amounts estimated by using the Langmuir plot were, respectively, $2.37 \times 10^{-4} \text{ mol/g}$, $2.49 \times 10^{-4} \text{ mol/g}$, and $3.59 \times 10^{-4} \text{ mol/g}$. The saturated adsorbed amounts corresponded to S_{BET} values of the titanium oxide nanoparticles.

Figure 9 shows adsorption isotherms of Evans blue, which is an anionic dye molecule. The saturated adsorbed amounts of Evans blue molecules of the nanoparticles were less than $2.5 \times 10^{-5} \text{ mol/g}$. According to the results presented in Figures 8 and 9, the cationic dye molecules interacted strongly with the surface of the titanium oxide nanoparticles obtained by heating the mixtures of ethylene glycol solution of TIP and NH_3 (aq). As presented in Figure 1(d), when the $[\text{NH}_3]$ value was 1 mol/L, the obtained nanoparticles were mixture of anatase TiO_2 and layered titanitic acid. In general, a layered titanitic acid structure shows the cationic ion exchange property. Therefore, an enhanced adsorption towards the cationic dye molecules on the nanoparticles

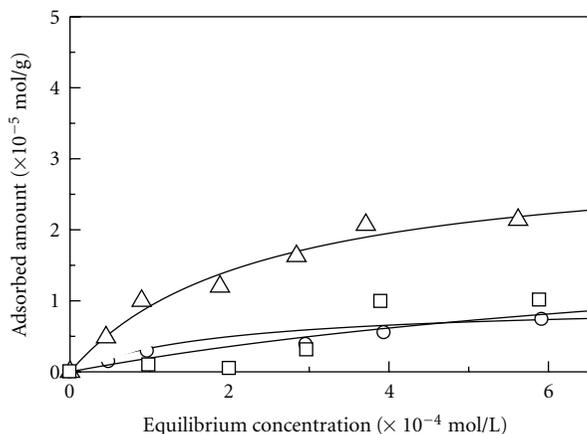


FIGURE 9: Adsorption isotherms of Evans blue on the titanium oxide nanoparticles in aqueous solution of dye. The concentrations of NH_3 (aq) used to prepare the titanium oxide nanoparticles were the following: \circ , 1 mol/L; \square , 0.2 mol/L; and \triangle , 0.1 mol/L.

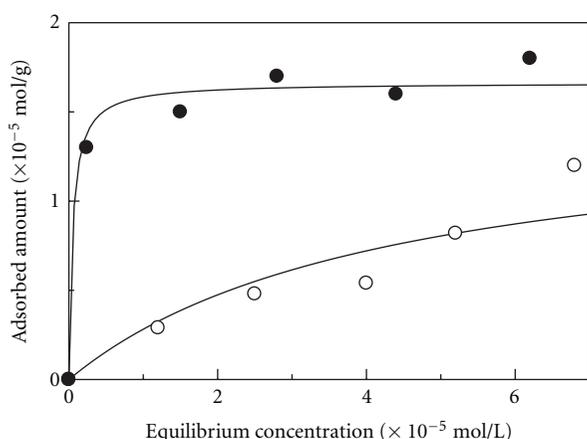


FIGURE 10: Adsorption isotherms of dye molecules on titanium oxide nanoparticles in aqueous solution of dye. The dye molecules were the following: \circ , methylene blue and \bullet , Evans blue. Titanium oxide nanoparticles were prepared by heating the mixture of TIP and H_2O at 368 K for 24 h.

corresponded to the presence of layered titanic acid structure in the obtained nanoparticles. On the other hand, although the XRD peaks of the nanoparticles prepared at $[\text{NH}_3] = 0.1$ mol/L as presented in Figure 1(a) can be assigned only to anatase TiO_2 , the obtained nanoparticles also showed the enhanced adsorption towards the cationic dye molecules. In this case, the layered titanic acid particles with very low degree of crystallization were included in the obtained nanoparticles so that the presence of the layered titanic acid phase cannot be detected by XRD. To examine the above consideration, the adsorption characteristics of conventional anatase TiO_2 particles, the dye adsorption isotherms of the particles were presented in Figure 10. The saturated adsorbed amounts of methylene blue and Evans blue were, respectively, 1.50×10^{-5} mol/g and 1.66×10^{-5} mol/g. In

this case, the adsorbed amount of Evans blue, an anionic dye molecule, was larger than that of methylene blue, a cationic dye molecule. This adsorption behavior was opposite to the titanium nanoparticles obtained from the ethylene glycol solution of TIP and NH_3 aqueous solution. Accordingly, the positively charged sites on the anatase particles such as Ti^{4+} ions played an important role in the adsorption of Evans blue molecules. Therefore, the adsorption behavior of the dye molecules depends strongly on the surface characteristics. Results show that the selective adsorption of the cationic dye molecules did not correspond to the anatase TiO_2 structure. The layered titanic acid structure is expected to play an important role in the selective adsorption of the cationic dye molecules. The hydrolysis reaction with a sufficient amount of NH_3 aqueous solution enabled formation of a composite of layered titanic acid structure and anatase TiO_2 , and it is considered that the structure contributed to the selective dye adsorption characteristics.

4. Conclusion

Transparent and stable sols of titanium oxide nanoparticles were obtained by heating a mixture of ethylene glycol solution of TIP and NH_3 aqueous solution at 368 K for 24 h. The concentration of NH_3 aqueous solution affected the structure of the obtained titanium oxide nanoparticles. When the concentration of NH_3 aqueous solution was 0.1 mol/L, the obtained nanoparticles were assigned to anatase TiO_2 according to the XRD pattern. When the concentration was higher than 0.2 mol/L, a mixture of anatase TiO_2 nanoparticles and layered titanic acid nanoparticles was obtained. The coordination of ethylene glycol and NH_3 molecules to Ti^{4+} ions played an important role in the formation of titanium oxide nanoparticles and their homogeneous dispersion in the sol. The obtained titanium oxide nanoparticles had a large specific surface area, which was larger than $350 \text{ m}^2/\text{g}$ because the aggregation of their nanoparticles was prevented by the coordination of NH_3 and ethylene glycol molecules. The obtained titanium oxide nanoparticles indicated an enhanced adsorption towards the cationic dye molecules. The selective adsorption corresponded to presence of the layered titanic acid on the nanoparticles. The high specific surface area also played an important role for the selective adsorption of the cationic dye molecules. Accordingly, the hydrolysis reaction of TIP with ethylene glycol and NH_3 enabled us to obtain stable sols of anatase TiO_2 and layered titanic acid nanoparticles with highly homogeneous dispersion. Furthermore, the obtained nanoparticles showed unique adsorption characteristics.

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