Preparation of Anatase Particles through Electro-Dialysis of TiCl_4 Aqueous Solution

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ABSTRACT

Anatase particles of titanium dioxide were prepared from TiCl_4 aqueous solution by using an electro-dialysis [ED] process. For the preparation of an aqueous solution of TiCl_4 precipitates, TiCl_4 liquid frozen in ice was transferred to a neck flask and then hydrolyzed using deionized [DI] H_2O . During the hydrolysis of the TiCl_4 solution at 0°C , a slurry solution of TiOCl_2 was obtained and the color changed from red to orange. The ED process was applied for the removal of chlorine content in the slurry solution. Two kinds of hydrolyzed slurry solution with lower $[\text{Ti}^{4+}]$ and higher $[\text{Ti}^{4+}]$ were sampled and the ED process was applied for the samples according to the removal time of $[\text{Cl}^-]$. With de-chlorination, the solution status changed from sol to gel and the color quickly changed to blue. Finally, white crystalline powders were formed and the phase was confirmed by XRD to be anatase crystallites. The morphology of the hydrous titania particles in the solution was observed by FE-SEM. The hydrous titania particles were nano-crystalline, and easily coagulated with drying.

Key words : Titanium tetrachloride, Anatase, Electrodialysis, Nano-particles, Anion membrane

1. Introduction

Because it is nontoxic, easy to fabricate, inexpensive, and chemically stable, TiO_2 has been widely investigated and used in materials over the past several decades. Synthesis of highly crystalline titania nano-particles with controlled crystal structure, morphology, and size has been a very active field in materials chemistry.¹⁻⁴⁾ In recent years, TiO_2 -based nano-materials have attracted significant research attention due to their broad applications in the fields of water and air purification, H_2 production, and photovoltaic and photo-electrochemical cells. TiO_2 is a promising material for photo-electrochemical energy production and as such is an attractive material for solar energy conversion and as an effective catalyst for photo-oxidizing of a variety of hazardous organic chemicals in air and in water at room temperature. Among three polymorphs, anatase (tetragonal, metastable), rutile (tetragonal, stable), and brookite (orthorhombic, metastable), the metastable anatase-type TiO_2 has been known to exhibit the highest photocatalytic activities¹⁾; this polymorph transforms into a thermodynamically stable rutile phase with heat treatment above 635°C , as was determined in a kinetic study on the transformation from anatase to rutile.⁴⁾ The phase transformation temperature of metastable inorganic materials is affected by their grain size, impurities, compositions, precursor materials,

processing, and by the nature and amount of dopants. Recently, intensive attention has been devoted to wet chemical routes to obtain nanometer-sized particles of inorganic materials. Preparations of fine TiO_2 powders and their precursors have been examined using several techniques.⁴⁻⁶⁾

In this study, an aqueous solution of TiOCl_2 was prepared by hydrolysis of TiCl_4 solution in ice water; then, an electro-dialysis [ED] process⁷⁻⁹⁾ was applied to the solution. The application of an ED process in a TiOCl_2 solution was very effective for the preparation of TiO_2 nano-particles without chlorine residue. The particle morphology of the prepared TiO_2 nano-particles was analyzed using FE-SEM. The slurry solution of TiO_2 nano-particles was filtered using DI H_2O and, finally, ethanol solution. The dry sample was used for XRD and FE-SEM analysis.

2. Experimental Procedure

2.1. Preparation of TiOCl_2 solution through hydrolysis

In the hydrolysis process, as shown in Fig. 1(a), TiCl_4 (99.0% purity, Sigma Aldrich) was carefully transferred to a neck flask under ice temperature and dissolved in deionized [DI] H_2O . The frozen TiCl_4 solution in a bottle was transferred to the reactor through a double tip cannula needle line under N_2 gas atmosphere. An inert atmosphere of pure N_2 gas was provided using a Schlenk line system. The TiCl_4 solution in the received bottle can be violently volatilized to HCl gas if the cover is opened in the air. In order to prevent a violent exothermic reaction with H_2O , the bottle was kept under ice temperature and N_2 atmosphere. We put a rubber septum cap into the bottle, which was kept under N_2 atmo-

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Fig. 1. (a) Experimental design of hydrolysis process for TiCl_4 solution. The inert atmosphere was controlled through a glove box and a Schlenk line. The main round flask was in an ice bucket. (b) The aqueous solution of TiCl_4 was hydrolyzed with DI H_2O in the flask, showing a red-yellowish color. (c) Reactor for ED process. The electrode is a Pt-coated Ti alloy. Through the AMV membrane, Cl^- ions are transferred to the right side compartment by DC power. (d) Total experimental design for the D-ED process.

sphere in a glove box. The rubber capped bottle was frozen in the refrigerator. Just before the TiCl_4 transfer to the reactor, the frozen bottle was taken out and put in an ice water bath; this was similar to the procedure used with the Dewar flask model,⁶⁾ which is shown in Fig. 1(a).

Hydrolysis of TiCl_4 solution

For the hydrolysis of the TiCl_4 solution, using a syringe needle, DI [deionized] water was slowly added dropwise under stirring through the flask septum. A liquid phase hydrolysis reaction of TiCl_4 was also carried out.⁶⁾ In Fig. 1(b), it can be seen that an orange color solution was obtained due to the formation of TiOCl_2 .^{6,10-13)} The addition of DI water to TiCl_4

solution induces a strong exothermic hydrolysis reaction of TiCl_4 , with the generation of HCl gas. Because of the highly exothermic reaction, the solution temperature quickly became hot. The overall process, such as the stirring speed and the addition of DI H_2O , was carefully controlled to maintain the reaction temperature in the salt-ice bath. TiCl_4 is known to react violently with water, releasing highly corrosive and toxic hydrogen chloride (HCl) gas.^{6,13,14)} The HCl gas pressure in the reactor was very strong, and so the septum rubber cap was tightly sealed to the flask neck with copper wire. It was also important to maintain appropriate N_2 gas pressure in the cannula line through the sep-

tum. In the reactor, N_2 gas has to be slowly injected in order to prevent the hydrolysis reaction. For the prevention of gas pub-up of the septum, the flask was frozen in a salt ice bath and the addition of H_2O was slowly controlled under stirring in an N_2 gas atmosphere. The transferred TiCl_4 solution was stirred for 20 min; then, DI H_2O was slowly injected into the reactor. The reaction with H_2O is very strong and exothermic. The reactor has to be strongly stirred and frozen using salt ice to prevent overpressure generation of HCl in the reactor. The starting precursor solution was TiCl_4 [Sigma Aldrich, 99.8%]. The stock solution of TiCl_4 was received in a bottle, which was frozen in salted ice water and transported to the flask reactor at 0°C . Pieces of block ice were added to the reactor to suppress fast hydrolysis when frozen water was slowly added to the flask reactor. The concentration of TiCl_4 was 2 mole/L; it was found that the stock solution could be kept for a year at room temperature without precipitation.

During hydrolysis, the solution color was red and then changed to orange with the increase of H_2O addition. At room temperature, the orange color solution was transferred to the ED [ElectroDialysis] process reactor for de-chlorination, as can be seen in Fig. 1(C). Anatase titania nano-crystallites were prepared using a low concentration of TiCl_4 in water, at a molar ratio of $\text{TiCl}_4/\text{H}_2\text{O} = 1/15$ and a high concentration of TiCl_4 ($\text{TiCl}_4/\text{H}_2\text{O} = 1/10$) in the temperature range of $40\text{--}60^\circ\text{C}$. Small, uniform, and yet size-tunable (5 - 10 nm) nano-crystalline TiO_2 (anatase) powders were prepared by electro-dialysis of TiOCl_2 in aqueous chloride solutions.^{7,9)}

The details of the experimental process are as follows:

- 1) septum rubber cap was attached to a TiCl_4 precursor bottle in a glove box under N_2 atmosphere using an ice bucket.
- 2) Using a Schlenk line system, septum rubbers were attached to the necks of the reactor flask through vacuum and filling of N_2 gas.
- 3) The frozen TiCl_4 bottle was moved to a salt-ice water bath and the TiCl_4 bottle was connected to the reactor flask neck using a Cannula line.
- 4) By controlling the N_2 gas pressure in the Schlenk line system, it was possible to transfer the TiCl_4 solution to the flask. Under N_2 gas in the reactor, DI H_2O was injected through another neck using a syringe. The reactor was rapidly stirred during the hydrolysis reaction.
- 5) After the termination of hydrolysis, the reaction precipitates at room temperature were poured into the ED reactor.

During the hydrolysis reaction, $[\text{Ti}^{4+}]$ was controlled at 0.5M by the addition of iced H_2O ; solution was stirred for an hour. The precipitation reaction occurred at room temperature. After the termination of the precipitation reaction, the slurries of the precipitates were moved to the ED reactor in order to remove Cl^- ions. After 10 minutes of ED process, the solution color changed from orange to blue and the sol-gel transition was simultaneously observed.

The DI water was purified by passing it through a PTFE filter (0.2 μm). After the de-chlorination, the precipitates were dried at 60°C for 12 h. In order to prevent the de-flocculation of the precipitates without Cl^- , the precipitates were washed using DI H_2O and ethanol.

2.2. ED reactor and Removal of Cl^- in Ti-OH-Cl solution

At room temperature, the mixture solution of Ti-OH-Cl was transferred to the reaction chamber, which had a cathode, as shown in Fig. 1(C); the ED process was performed for the removal of Cl^- ions, as has been previously reported.^{7,8)} With the progress of the ED reaction, it was possible to observe gel-like particles in the transparent solution; with the increase of de-chlorination, the slurry solution became highly viscous. The color quickly changed to orange red, yellowish, and blue with the increase of de-chlorination; finally, solid white particles were visible after an hour with the appearance of the above-mentioned gel-like particles. With the increase of the white solid particles, the slurry solution became less viscous. After a half day of de-chlorination, the current value of the DC power supply dropped to under 0.03 A, which was taken as an indication of ED reaction completion. After the termination of the ED reaction, the hydrous titania precipitates in the main reactor were transferred to a beaker and stirred for several hours. The hydrous titania precipitates were washed in a vacuum filter using DI H_2O and, finally, methyl alcohol solution for the control of particle disintegration. The wet slurries were dried at 70°C overnight, and the crystal phase and microstructure were characterized by XRD and FE-SEM, respectively.

During the ED process, the O^- ions from H_2O reacted with TiOCl_2 with no further hydrolysis reaction and so the TiO_2 precipitates were able to form. Normally, above 65°C anatase type TiO_2 is formed, but below 65°C rutile TiO_2 is formed. At low temperature, the precipitation reaction is so slow that it forms rutile crystallites, but with an increase of the reaction temperature above 65°C , the precipitation kinetics is rapid enough to form anatase crystallites.^{13,14)} Through the ED process that is used to remove Cl^- ions in aqueous TiOCl_2 solution, sol – gel precipitates were formed and then changed to anatase phase. The experimental details are as follows:

Figure 1(d) shows the Electro-dialysis [ED] process system in which Cl^- ions are removed through an anion membrane [AMV]. The sol-gel phase formation of titanium hydroxide in the left chamber is affected by the decrease of $[\text{Cl}^-]$. During the ED process, the formation of crystalline and/or non-crystalline phase was influenced by the reaction temperature, which was controlled at $< 60^\circ\text{C}$ in order to prevent the degradation of the membrane. The TiOCl_2 solution in the ED reactor showed a color change from red to white with de-chlorination. After ten minutes of ED voltage application, the color changed from orange red to yellow, and then a blue color appeared, as shown in Fig. 1(c). After 30 min, the color changed to white. The phase status changed

from sol to gel; then, nano-crystalline particles were confirmed with the removal of Cl^- . With the reaction time of de-chlorination the quantity of the solid phase increased and the solid paste gradually became crystalline.

2.3. Characterization

XRD [Bruker, M18XCE] was used for the characterization of the dried powders after the termination of the ED process. The microstructure of the sintered body was investigated using FE-SEM [Hitachi, S-4800].

3. Results and Discussion

3.1. Preparation of anatase nanocrystals from TiCl_4

In normal NH_4OH precipitation from aqueous solution of TiCl_4 , the precipitates show a non-crystalline phase, even after they are heat treated at 100°C for 6 h.¹³⁻¹⁵⁾ In order to obtain the crystal phase, the precipitates have to be calcined at above 400°C . If an aqueous solution of TiOCl_2 is stirred at 100°C , anatase crystallites are formed without the formation of the hydrolyzed phase of $\text{Ti}(\text{OH})_4$.

Originally, transparent TiCl_4 solution is a material that has a large vapor pressure at room temperature and hydrolyzes readily by reacting with water from the air. When a large amount of H_2O was added to the transparent TiCl_4 , a red hydroxide material was formed and then *in situ* converted into an aqueous TiOCl_2 solution of hard yellowish orange color. During the preparation process of the aqueous TiOCl_2 solution, there was a dissociation of TiCl_4 into the yellow hydroxide and HCl with the addition of a large amount of H_2O into TiCl_4 .

In the ED process, using an anion membrane [AMV, Selemion Asahi Chemical], titania nano-crystallites formed below 60°C . De-chlorination from the hydrolyzed compound of Ti-OH-Cl was done by Diffusion ElectroDialysis [D-ED]. With applied DC [Direct Current] bias, the Cl^- ions in the Ti-OH-Cl reactor compartment moved to the surface of the anion membrane, AMV, and diffused to the other side compartment of H_2O , which became an HCl solution due to the increase of $[\text{Cl}^-]$. Because of the exothermic reaction between H_2O and Cl^- ions, the temperature increased abruptly. A solution temperature above 60°C can deteriorate the carbohydrate polymer membrane [AMV], and so the HCl solution was periodically replaced with pure water in order to cool down the membrane, as shown in Fig. 1(D). If we use a fluorinated ion-exchange membrane such as a Flemion F-8080, [Asahi Glass Japan] or a Nafion membrane

[Aldrich],^{16,17)} the temperature of the ED reaction can be allowed to increase above 60°C . Fluorinated membranes are tougher and more resistant to heat and chemical attack by Cl^- ions than the Selemion AMV membrane.

3.2 XRD analysis

Figure 2 shows the XRD patterns of the samples. Anatase phases of nano-crystalline TiO_2 powders were confirmed in the samples, which were prepared by D-ED process of TiO-Cl_2 in aqueous chloride solutions. Small, uniform, and yet size-tunable (5 - 10 nm) anatase titania nano-crystallites were prepared for the samples using a low concentration of TiCl_4 in H_2O (i.e., at molar ratios of $\text{TiCl}_4/\text{H}_2\text{O} \leq 1/15$) and a high concentration of TiCl_4 in H_2O (i.e., at molar ratios of $\text{TiCl}_4/\text{H}_2\text{O} \leq 1/10$) in the temperature range of $40 - 60^\circ\text{C}$. The formation of anatase phase seems to result from the de-chlorination, which is enforced by DC power.

3.3. Microstructure of Anatase powders

Figure 3 show the microstructure of the samples, obtained using FE-SEM, with sample groups of TiO_2 -1 and TiO_2 -2 for low concentration of TiO_2 and high concentration of TiO_2 in the ED process, respectively. During the ED process, the precipitates for TiO_2 -1 were picked up with time from 30 min, 1 h, 2 h, 4 h, 6 h, and 12 h for samples of m001, m002, m003, m004, m005 and m006, respectively. In the TiO_2 -2 samples, precipitates were taken out at times of 30 min, 2 h, 6 h, and 12 h for samples of m001, m002, m003, and m004, respectively.

In Fig. 3(A), the nano-crystallite size (3.5 nm) of TiO_2 -2 can be seen to be slightly larger than that (3.0 nm) of TiO_2 -1 until the de-chlorination reaction has proceeded for two hours. That is, the crystal growth of the nano-crystallites was greatly accelerated by the stronger hydrolysis in the higher concentration sample.⁶⁾ It is known that a higher concentration in the solution induces an acceleration of the crystal growth. With the increase of the de-chlorination time from 30 min and 12 h, it can be seen in Fig. 3(b) that the crystal growth of the TiO_2 -2 samples has high concen-

Fig. 2. XRD analysis for TiO_2 -1 and TiO_2 -2 samples for the higher concentration and the dilute concentration, respectively.

Fig. 3. Photographs of the samples of high concentration, TiO_2 -1, and low concentration, TiO_2 -2. (a) Crystal growth in TiO_2 -1 with ED times of m001 and m005, and crystal growth in TiO_2 -2 with ED times of m001 and m003. (b) Crystal growth in TiO_2 -2 with ED times of m001, m002, m003, and m004. (c) Crystal growth in TiO_2 -1 with ED times of m001, m003, m004, and m006. (d) Crystal growth in TiO_2 -1 with ED times of m002, m003, m005, and m006.

tration. The crystalline size of TiO_2 -m004 is 4.0 nm, as can be seen in Fig. 3(b), which is larger than that (3.5 nm) of TiO_2 -m001 in Fig. 3(a).

Figure 3(c) shows the crystal growing for TiO_2 -1 samples with ED reaction time, and the crystallite sizes are 3.0 nm and 4.0 nm for TiO_2 -1-m001 and TiO_2 -1-m004, respectively. In Fig. 3(d), for another sample of TiO_2 -1, the crystallite sizes are 3.3 nm and 4.3 nm for TiO_2 -1-m002 and TiO_2 -1-m005, respectively.

Figure 4 shows the crystallite size variation with the ED reaction time for the sample group of low concentration and for the high concentration group, namely groups TiO_2 -1 and TiO_2 -2, respectively. The variation of the crystal growth rate of the dilute sample, TiO_2 -1, is larger than that of the concentrated sample, TiO_2 -2. In the D-ED derived crystallites of TiO_2 , the formation of the anatase phase seems to be caused by the de-chlorination process. With the appearance of anatase crystallites, the crystal growth is accelerated by the interface reaction between TiO_2 crystal nuclei and the solution ion concentrations, such as the concentrations of $[\text{Ti}^{4+}]$, $[\text{Cl}^-]$, $[\text{O}^{2-}]$, $[\text{H}^+]$, and $[\text{OH}^-]$. With the decrease of $[\text{Cl}^-]$,

Fig. 4. Crystal growth with time during ED process.

TiO_2 crystal growth is accelerated due to the presence of complex Ti-O-Cl nuclei. This reaction will be enhanced in dilute concentrations of Cl^- . In the higher concentration sample of TiO_2 -2, the amount of $[\text{Cl}^-]$ is higher than that in

the TiO_2 -1 samples, and so this sample shows a low chance of crystal growth. The growth is proportional to the local super-saturation. De-chlorination is enforced by the DC power supply and the ability of the diffusion membrane to perform Cl^- ion transfer. In this D-ED process using an AMV membrane, the reaction temperature was controlled so that it stayed below 60°C . The obtained powder slurry was filtered using DI water and ethanol washing. For the dry sample powders, the presence of anatase crystallite was confirmed by XRD analysis, as can be seen in Fig. 2.

3.4. Discussion

Figure 4 shows the typical crystal growth of TiO_2 with the removal time of Cl^- ions during the de-chlorination of precipitates in the D-ED reactor after solution precipitation. The crystal growth of TiO_2 in the Ti-OH-Cl solution increased with the de-chlorination of the slurry solution. Of course, there can be several other factors involved such as the Cl^- ion detachment rate from the Ti-OH-Cl complex compound, the ion transfer rate in H_2O , and the Cl^- ion diffusion rate through the AMV membrane. Details on the relative influence of each factor¹⁸⁻²³⁾ will be determined and provided in another report. In the normal hydrolysis of TiCl_4 , precipitates of the Ti-OH-Cl compound are formed. In this D-ED process to remove Cl^- ions in the aqueous solution of the Ti-OH-Cl compound, the elimination of Cl^- ions in the aqueous solution is quickly accomplished. In the next step, the Cl^- ions in the Ti-OH-Cl compound are gradually detached and transferred to the anion reactor through the anion membrane, AMV, by the application of DC current. The existence is confirmed of octahedral hydroxochloro complexes of the type $[\text{Ti}(\text{OH})_a\text{Cl}_b(\text{OH}_2)_c]^{(4-a-b)+}$, where $a + b + c = 6$, and a and b depend on the acidity and the concentration of Cl^- in the solution.¹²⁾ In this D-ED process, the DC power enforces the detachment of Cl^- ions in the Ti-OH-Cl complexes; this may be the rate limiting step in the transfer of Cl^- ions to the anion compartment through the AMV membrane. With the removal of Cl^- ions, the Cl^- ion concentration decreases and the reaction requires higher enforcing power for Cl^- ion detachment in the complex. In our experimental design, we decided that the removal of Cl^- ions had finished when the current value was under 0.03 A in the DC power supply.

4. Conclusions

Using the D-ED process, mono-dispersed ultrafine TiO_2 particles with diameters of 3 - 4.5 nm were obtained through de-chlorination from aqueous TiOCl_2 solution with a 0.5M Ti^{4+} concentration prepared by diluting TiCl_4 in a homogeneous spontaneous precipitation process. The de-chlorinated precipitates were dried at 60°C ; through analysis using XRD and FE-SEM, the phase was found to be anatase nano-crystallites. With increased de-chlorination time, the crystal growth rate of TiO_2 in the lower concentration sample of Ti^{4+} ions was found to be larger than that of the

higher concentration sample of Ti^{4+} ions.

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