



Effect of solvent species inside wet gel on fabrication of titania nanoparticle by supercritical carbon dioxide drying



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ABSTRACT

Titania nanoparticles were fabricated by sol–gel reaction and supercritical carbon dioxide drying. The solvent inside wet gel obtained from sol–gel reaction was exchanged to organic solvents, acetone, 1-butanol and *N*-methylpyrrolidone before the supercritical drying. The wet gels exchanged by organic solvents were dried in supercritical carbon dioxide at 313 K and 10.0 and 20.0 MPa. It is found that the structures of the titania nanoparticles were like nano-needle. The minor-axis sizes of the nano-needle titania nanoparticles were measured by a scanning electron microscope observation. The wet gel exchanged by 1-butanol results in the smallest minor-axis of titania nanoparticles, 97 nm in the supercritical drying at 313 K and 20.0 MPa. The drying of the wet gel exchanged with *N*-methylpyrrolidone exhibit the reduction of the minor-axis of titania nanoparticle larger than those with acetone and 1-butanol, 181 to 103 nm by increase of pressure, 10.0 to 20.0 MPa.

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1. Introduction

Titania (TiO₂) nanoparticle obtained from supercritical drying has been one of attractive materials in various industrial fields due to the high surface area and large pore volume. A development of high porous TiO₂ is required for the exploitations of photocatalyst, semiconductor in solar cells [1–3] and catalyst support in fuel cells [4–7]. Hasa et al. [4] have studied the fabrication of Pt–TiO₂ binary electrodes for direct alcohol fuel cells (DAFCs). It was reported that the current density of the fuel cell using Pt–TiO₂ electrode on the methanol electro-oxidation was around 4 times higher than that in case of pure Pt electrode. The addition of TiO₂ in the catalyst is expected to prevent the aggregation of Pt particles on the catalyst and then increase the reacting surface area of the catalyst. Iwai et al. [2,3] have fabricated the needle-like TiO₂ for the electrode film of dye-sensitized solar cell (DSSC). It was reported that the DSSC with the needle-like TiO₂ electrode results in the electrical power around 1.5 times as high as that fabricated with the commercial TiO₂ nanoparticles [3]. The effective utilization of TiO₂ nanoparticle on the applications as above would require the controlling the morphologies of nano- or micro-particles leading to their higher surface area.

Nanostructures of TiO₂ are fabricated by a sol–gel reaction with titanium alkoxide and supercritical carbon dioxide drying. In the

sol–gel reaction, the hydrolysis and polymerization of the titanium alkoxide results in the formation of wet gel of TiO₂. The wet gel is dried in supercritical carbon dioxide for the production of the TiO₂ nanostructure consequently. Supercritical carbon dioxide has the unique properties, such as high dissolution ability, high diffusivity and low viscosity. Many attractive techniques in the material process using supercritical carbon dioxide have been developed, for example rapid expansion of supercritical solution, supercritical antisolvent [8], supercritical solution impregnation [9] and supercritical drying [10,11]. The supercritical carbon dioxide drying allow to remove the solvent from the wet gel without the collapse of the structured – materials in nano – or micro scale. For supercritical carbon dioxide + organic solvent system, the homogeneous phase can be formed at the pressure over the critical point of this binary system. Therefore, it is possible to conduct the drying process without interfacial tension by using supercritical carbon dioxide.

The research groups of Sui et al. have reported the synthesis of titania nanostructures in supercritical carbon dioxide [12–14]. Nano-needle TiO₂ is fabricated by sol–gel reaction using titanium tetrabutoxide (TBO) and acetic acid (HAC). It is reported that a high molar ratio of HAC to titanium alkoxide can form the morphology change of TiO₂ nanoparticles like the sphere and needle when using as the precursor [12]. Supercritical drying has been conducted with exchanged solvent inside the wet gel for the formation of homogeneous phase for carbon dioxide + the solvent system [2,3]. The mass transfer of the solvent from wet gel to carbon dioxide phase would also affect the consequent structure after the supercritical drying.

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Table 1
Properties of organic solvents at 313 K.

Solvent	Vapor pressure (kPa)	Surface tension (mN m ⁻¹)	Critical Pressure for CO ₂ + solvent (MPa)
Acetone	58 [15]	21.2 [16]	8.1 [21]
1-Butanol	2.6 [17]	22.84 [18]	8.2 [22]
NMP	0.139 [19]	40.27 [20]	9.5 [23]

There is few literature data concerning the effect of the solvent inside the wet gel on the consequent structure after the supercritical drying. This can be very important and useful knowledge for the design of the structure of TiO₂ nanostructure fabricated by supercritical drying.

Nano-needle of TiO₂ was fabricated by supercritical carbon dioxide drying for the wet gel with exchanged various organic solvents in this work. The minor-axis size of the nano-needle TiO₂ is investigated by relating with the species of organic solvent exchanged inside the wet gel. Thin film of TiO₂ on carbon sheet was also fabricated using the nano-needles. The effect of the minor-axis of TiO₂ nano-needle on the film roughness is discussed.

2. Experiments

2.1. Chemicals

Titanium tetrabutoxide (97.0%) from KANTO CHEMICAL CO., INC and acetic acid (99.9%) from Wako Pure Chemical Industries, Ltd. were used for sol–gel reaction. Organic solvents used for exchanging solvent inside wet gel are acetone (99.9%), 1-butanol (99.0%) and *N*-Methyl-2-pyrrolidone (NMP) (99.0%) from Wako Pure Chemical Industries, Ltd. Table 1 shows the properties of the organic solvents. Carbon dioxide (99.95%) was supplied from Fujii Bussan Co. Ltd. Carbon sheet (CS) from Toray Industries, Inc was used as substrate for TiO₂ thin film. Titanium oxide (IV) with nano-sphere of 150 nm from Wako Pure Chemical Industries, Ltd. was used for fabrication of the TiO₂ thin film for comparison of roughness with nano-needle TiO₂ thin film.

2.2. Synthesis of TiO₂ wet gel

The wet gel of TiO₂ was synthesized by sol–gel reaction of titanium tetrabutoxide (TBO) with acetic acid (HAc). Known amounts of TBO and HAc were reacted at 333 K for 2 h. The initial molar ratio of HAc to TBO was 10. After the reaction time, the white TiO₂ sol was obtained. The TiO₂ wet gel like viscous liquid was obtained after cooling the sol at room temperature for 3 h. The wet gel was in organic solvent for 24 h in order to exchange the solvent of sol to the organic solvent. The amount of organic solvent used for the exchanging the solvent was equal to that of TiO₂ sol. The TiO₂ wet gel was separated consequently from the supernatant solution of the sol.

2.3. Supercritical carbon dioxide drying

A schematic diagram of supercritical drying apparatus is given in Fig. 1. The supercritical drying in this work was conducted by a continuous system using the procedure described below. This apparatus is composed of CO₂ supply part, high-pressure cell and depressurization part. The volume of high-pressure cell was 80 mL. The wet gel of TiO₂ after exchanging the solvent was installed in the high-pressure cell before starting the experiments. Carbon dioxide from cylinder was passed through silica gel cell in order to remove the trace amount of water in carbon dioxide and then was liquefied in cooler. The liquefied carbon dioxide was pressurized by pump. The pressurized carbon dioxide was supercritical state by feeding into the high-pressure cell in which the temperature

was controlled using air thermostat at the desired condition. The pressure of drying system was controlled by back-pressure regulator. The supercritical drying was conducted at the 313 K and 10.0 and 20.0 MPa over the critical pressure for carbon dioxide + acetone, 1-butanol or NMP binary system as given in Table 1. These temperatures and pressures allow to form the homogeneous phase for carbon dioxide + organic solvent inside the TiO₂ wet gel in order to allow the drying without the phase interface between supercritical carbon dioxide and liquid phases. The dryings were conducted for 3 h in case of acetone and 1-butanol and 6 h in case of NMP at flow rate of carbon dioxide 100 mL min⁻¹. After the supercritical drying, the system was depressurized at 0.13 MPa min⁻¹. The white powder of nanostructured TiO₂ was obtained after the depressurization. The synthesized TiO₂ nanoparticle from supercritical drying was calcined at 773 K for 2 h for the crystallization. The powder of TiO₂ nanoparticle after the calcination was used for fabrication of TiO₂ thin film.

2.4. Fabrication of TiO₂ thin film

The calcined TiO₂ was added into the solution of ethanol without grinding and TBO and then mixed at 333 K for 2 h. The mixture was also sonicated for 15 min for the formation of TiO₂ dispersed solution in order to prevent the aggregation of TiO₂ nanoparticles. The added amount of ethanol was 10 mL g⁻¹-TiO₂. In this work, TBO was added as a binder between TiO₂ and CS substrate. The added amount of TBO was 0.5 g to 1 g TiO₂. The deposition of TiO₂ onto CS substrate in 15 mm × 15 mm was conducted by immersing CS substrate into the dispersed solution. The thin film of TiO₂ was formed after atmospheric drying 373 K for 1 h.

2.5. Analysis of TiO₂ nanoparticle

The structure of TiO₂ nanoparticle before the calcination was observed by Scanning Electric Microscope (SEM) (JEOL, JGM-6000). The TiO₂ nanoparticles were sputter-coated by Pt and Pd priori to SEM observation. The minor-axis size of TiO₂ nano-needle was also measured by the SEM observations. The value of minor-axis size of TiO₂ was determined from a median size for 600 samples in each SEM image for the four images to know the cumulative size

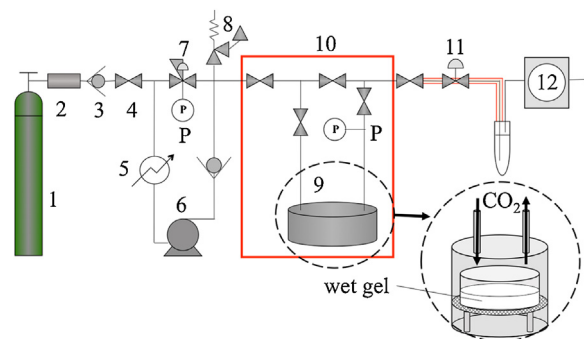


Fig. 1. Set up for supercritical carbon dioxide drying. 1; CO₂ cylinder 2; silica gel cell 3; check valve 4; stop valve 5; cooler 6; pump 7; back pressure regulator 8; safety valve 9; high-pressure cell 10; air thermostat 11; expansion valve 12; wet type gas flow meter P; pressure gauge.

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