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Preparation of thick TiO_2 film with large surface area using aqueous sol with poly(ethylene glycol)

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TiO_2 which is well known as a metal oxide semiconductor, has been employed in many industrial applications for its fine physical, chemical and optical properties. Recently, porous and nanostructured TiO_2 films have been successfully developed for photocatalysts [1, 2] and dye-sensitized solar cells [3, 4] with high performance due to large surface area of the films. For high performance, the film requires increased thickness as well as specific surface area. Generally, the thickness of the film deposited on a substrate by one run of dip-coating using the sol-gel derived solution was limited to 0.1–0.2 μm [5]. Although films with thickness of more than 1 μm can be prepared by repeating the coating cycle, it is not a practical process from the viewpoint of cost and energy efficiency. We have developed nanocrystalline-nanoporous TiO_2 films by the chemically modified alkoxide method [1, 2]. For this method, the pore size of TiO_2 films was controllable by changing the poly(ethylene glycol) (PEG) concentration in the dip-coating solution. The pores in the film were formed by the combustion of PEG by heating to over 400 °C. And also, we reported the TiO_2 film prepared using TiO_2 colloidal particles dispersed in water, which was obtained by hydrolyzing titanium (IV) isopropoxide, was very porous [6]. The polymer addition to the solution is usually utilized to adjust the viscosity of the solution. In the dip-coating technique, the film thickness increases in proportion to the viscosity of the coating solution. The combination of the TiO_2 sol and PEG is expected to allow preparation of porous and thick TiO_2 film. In this paper, the addition of PEG to the dip-coating solution, which is an aqueous sol of colloidal TiO_2 particles, is discussed. The effects of the addition of polymer to the TiO_2 sol on the thickness and microstructure of the resultant film are investigated.

The dip-coating solutions were prepared by the following method. The diluted solution of titanium (IV) isopropoxide (57×10^{-6} m^3) with isopropanol (50×10^{-6} m^3) was poured into a dropping funnel. The alkoxide solution was slowly dropped into the mixed solution of distilled water (300×10^{-6} m^3) and several different amounts of PEG (mean molecular weight = 2000, 0–15 g) under stirring with magnetic stirrer. A white suspension was obtained. A small quantity of concentrated nitric acid was added to the suspension and then heated at 80 °C with strong stirring to remove organic solvent. During stirring at 80 °C for 8 h, the opaque suspension changed gradually to clear sol by peptization. The formed clear sol was concentrated to a fixed volume (10^{-4} m^3) with heating at the same temperature.

The solutions were clear sol without any precipitates, although the solutions contained a large amount of PEG. The viscosity of the dip-coating solutions is very important because film thickness depends on the viscosity of the solution at a constant pulling rate of a substrate. The coefficient of viscosity of the dip-coating

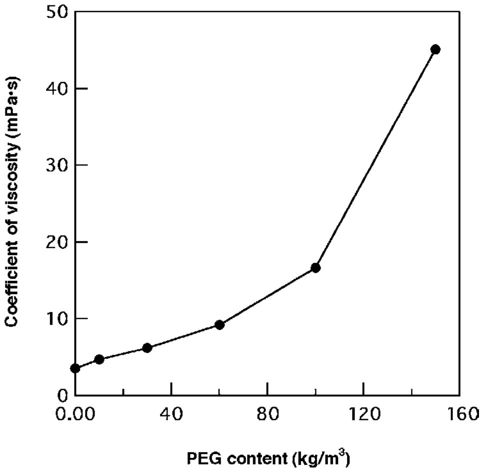

Figure 1 The relationship between the viscosity and PEG content of the solution.

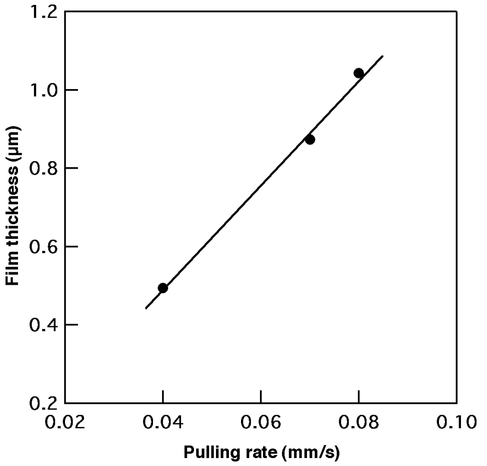

Figure 2 The relationship between the film thickness and the substrate pulling rate.

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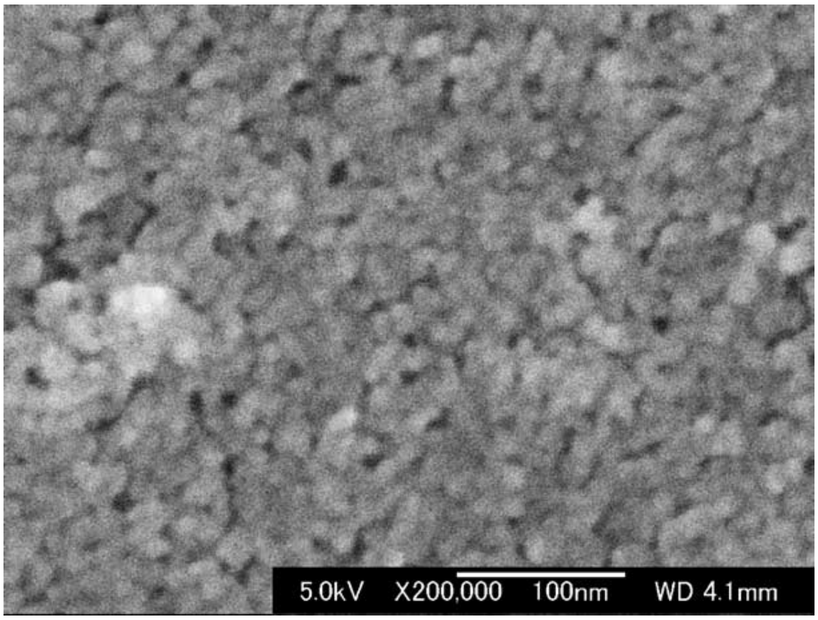

Figure 3 SEM photograph of the surface of TiO_2 film prepared by dip-coating with a pulling rate of 0.08 mm/s using the solution containing 150 kg/m^3 of PEG.

solutions was measured using an Ostwald viscometer at 25 °C. Fig. 1 shows the change of the coefficient of viscosity of the solutions with PEG content. The viscosity of the solutions increased remarkably with the increase in PEG content.

The TiO_2 films were prepared by dip-coating of glass substrates with different pulling rates using the most viscous solution containing 150 kg/m^3 of PEG. The TiO_2 films were prepared dipping a glass substrate (38 mm × 26 mm × 1 mm) into the dip-coating solution. The glass substrate was then withdrawn from the solution with the fixed rate, followed by drying at 80 °C for 15 min and heating up to 500 °C for 30 min in an electric furnace. All films prepared on the glass substrates were transparent, uniform and crack-free. The thickness of the films was measured by the SEM of cross-sections. Fig. 2 shows the pulling rate dependence of the thickness of the TiO_2 film. The maximum thickness of the film obtained by one-run dip-coating was ca. 1 μm.

Fig. 3 shows the SEM photograph of the surface of the 1 μm-thick TiO_2 film deposited on the substrate. From this observation, it is obvious that the film is an aggregate of TiO_2 particles with a diameter of ca. 20 nm and that interstices between the particles are common. The crystal structure of the film was clarified to be a single phase of anatase from XRD measurements. The crystallite size of the film calculated using Scherrer's equation was 6.5 nm. The crystallite size is in disagreement with the particle size from SEM observation. It is considered that the TiO_2 particles are polycrystals.

BET surface area and pore size distribution of the film were estimated by measuring N_2 adsorption-desorption at 77 K using 30 glass substrates (24 mm × 5 mm × 0.13–0.17 mm) coated with the film on both sides, since the weight of a single film on a substrate was too small to be measured. The N_2 adsorption and desorption isotherms showed isotherms of type IV with hysteresis loop as shown in Fig. 4. The hysteresis loop indicates mesopores exist in the film. Pore size distribution based on desorption isotherm and pore volume were calculated by the Dollimore and Heal method [7, 8]. Fig. 5 shows the pore size distribution of the 1 μm-thick film. The pore sizes were in the range of about 2 to 5 nm in radius and the peak was 3.5 nm. The specific surface area of the 1 μm-thick film was 111 m^2/g. The pore volume of the film was 395 mm^3/g. The porosity of the film, which was calculated using the pore volume and the density of anatase, was 63%. The nanometer sized pores were considered to form as the result of vaporization of water as the disperse phase and combustion of PEG during heat treatment.

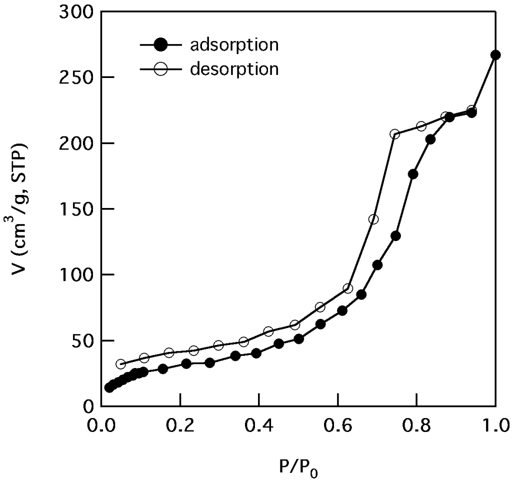

Figure 4 N_2 adsorption and desorption isotherms of the 1 μm-thick TiO_2 film.

The porous and thick film of TiO_2 was successfully prepared by the addition of PEG to the sol of TiO_2. The addition of PEG to the sol caused increase in thickness of the film coated on the substrate by increase in the viscosity of the sol. In general, cracking and detachment from the substrate during the heating process can easily occur in the thicker film coated on the substrate. In this

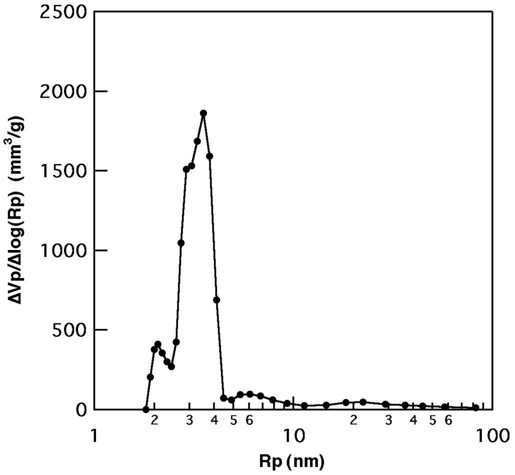

Figure 5 Pore size distribution of the 1 μm-thick TiO_2 film.

method, however, these damages were prevented by the addition of PEG to the sol. It is considered that the stress induced by the changing volume of the film during the heating process is relaxed by the plasticity provided to the film by the PEG addition. Simultaneously, the PEG addition was effective for keeping the porosity of the TiO_2 film. It suggested that the PEG addition suppressed the sintering between the TiO_2 particles, which may be attributed to an interaction between the colloidal particles and PEG adsorbed on them.

The nanoporous and thick TiO_2 film has been prepared by the dip-coating technique using the aqueous TiO_2 sol containing PEG. Film thickness can be controlled by the PEG concentration and pulling rate. The maximum thickness of the film prepared by one run dip-coating reached over 1 μm. The thick film was uniform and transparent with the porosity of 63%. The film with high surface area (111 m^2/g) consisted of aggregated TiO_2 particles in a diameter of 20 nm and pores with diameters of about 7 nm. PEG was found to have some positive effects on the preparation of the nanoporous and thick TiO_2 films.

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