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High Quality Monodispersed Oxide Nanoparticles Prepared by the Liquid Phase Deposition Method in Aqueous Polymer Solution

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Monodispersed TiO_2 nanoparticles were synthesized by the LPD process using polymer aqueous solution of polyethyleneglycol (PEG) in order to control reactivity of metal-fluoro complex and size of deposited TiO_2 particles. Monodispersed well-crystallized anatase particles are found after several minutes and easily separated from the reaction solution. The particle size of obtained samples ranged from ca. 3-5 nm with around 10% of standard deviation values. The synthesizing method presents a new route for preparing well-crystallized metal oxide nanopartcles with potential applications at an ambient condition.

Introduction

Nanocrystalline metal oxides have potential applications in modern technologies, such as solar energy conversion, batteries, catalysis, magnetic materials, and ductile ceramics etc. (1-7). In particular, titanium dioxide (TiO_2) nanocrystalline has attracted increasing attention due to its properties and utilizations, such as photocatalysts, photovoltaics, gas sensors and electrochromic display devices (8-14). However, it is necessary to control crystallinity and particle size of the particles for use in optical and energy conversion devices (15,16). Numerous studies of the preparation of TiO_2 particles and thin films have been carried out, and several kinds of solution reactions have been studied to prepare nanocrystalline oxides. In particular, sol-gel methods using hydrolysis of metal alkoxides or halides are popular. However, these methods often employ high temperature processing around 400-500ºC in order to avoid poor crystallinity, which can result in poor and/or inadequate electronic properties.

We have been studied a novel aqueous solution process for preparing various kinds of metal oxides thin films and their high dimension structured nanoceramics by the Liquid Phase Deposition (LPD) method. In LPD, the hydrolysis equilibrium reaction (ligand-exchange reaction) of metal-fluoro complex ($MF_x^{(x-2n)-}$) as well as an F^- consumption reaction with boric acid (H_3BO_3) or aluminum metal as a F^- scavenger (17-20). In the solution, metal-fluoro complex species are hydrolyzed with water (eq.1) and fluoride is taken up by boric acid (eq.2).

$$MF_x^{(x-2n)-} + nH_2O = MO_n + xF^- + 2nH^+ \quad [1]$$

$$H_3BO_3 + 4HF = BF_4^- + H_3O^+ + 2H_2O \quad [2]$$

LPD relies on the chemical equilibrium between the metal-fluoro complex and metal oxides by the minute energy difference in the aqueous solution at room temperature, which is one of typical soft solution process in the homogeneously mixed system (21,22). Therefore, we can apply the various kinds of substrate materials, such as glass, ceramics, metals, and polymers. According to our studies, nanoscale oxide thin films can be formed due to the small mean free path of the dissolved species (18, 19). Nano-sized particles of metal oxides can even be synthesized in reverse micelles, which have diameters less than 10 nm (23, 24).

In this study, we investigated the use of LPD with hydrophilic polymer, polyethyleneglycol (PEG), to make monodispersed and crystalline titanium oxide nanoparticles under ambient condition. Since PEG concentrations can range from trace to its solubility in aqueous system at will, a hetero energy level of molecular scale formed between polymer and metal-fluoro complex which causes nucleation of the metal oxides. Dependence of the PEG on reaction rate, particle size, and crystallinity are discussed.

Experimental

Sample Preparation

Ammonium hexafluorotitanate, $(NH_4)_2TiF_6$ (Morita Chemical Industries Co. Ltd.) and boric acid, H_3BO_3 (Nacalai Tesque Inc.) were prepeard in ion–exchanged water to give concentrations of 0.5 mol dm^{-3}, respectively. As a modifying species for metal-fluoro complex, polyethyleneglycol (PEG) with different molecular weights, purchased from Nacalai Tesque Inc., were used. Molecular weights of used samples were *ca.*200 and *ca.*600, PEG 200 and PEG 600, respectively. Aqueous $(NH_4)_2TiF_6$ solution and H_3BO_3 were sequentially added into aqueous PEG solution and continuously stirred for several minutes. The mixed solutions were used as a reaction system, whose final concentration was 0.02 mol dm^{-3} $(NH_4)_2TiF_6$, 0.2 mol dm^{-3} H_3BO_3 and 0.5-3.0 mol dm^{-3} PEG. Subsequently, the mixed solution was kept at 303 K for 20 hrs and then centrifuged at 12000 rpm for 20 minutes. The surpernatant was decantated carefully, and the precipitate was resuspended using distilled water and ultrasonication is to remove residual PEG and soluble species adsorbed on the sample surfaces. This treatment procedure was repeated three times. The obtained white powders were dried in a vacuum chamber at ambient temperature.

Characterization

The microstructure of the obtained TiO_2 were examined using a JEM-2010(JEOL) by transmission electron microscope. The accelerating voltage was 200 kV, and the point-to -point resolution was 0.19 nm. Diffraction patterns were calibrated by analyzing patterns obtained using a single crystalline Au thin film standard. X-ray diffraction patterns were collected using a Rigaku RINT-TTR/S2 X-ray diffractometer equipped with a cupper tube and using an acceleration voltage of 50kV and current of 300mA. TG-DTA analysis was carried from room temperature to 823K at 20K/min using a Rigaku TG-8120 in order to confirm dehydration and phase transitions. Raman spectra were collected using a Horiba T-64000 Monochromator. The excitation source was 532 nm SHG of Nd-YVO_4 laser. Raman spectra were calibrated from spectra collected using Si powder standard.

Results and Discussion

To prepare nanosized TiO_2 particles, the host aqueous solution of $(NH_4)_2TiF_6$ was dissolved into the guest solution of PEG. After adding the metal-fluoro complex solution, the mixture was still transparent, which indicated that the metal-fluoro complex was stable and did not hydrolyze in aqueous PEG. Subsequently, solution was mixed with H_3BO_3 aq., which act as a fluoride scavenger. Then, the solution was quickly whitened within 10 minutes, which indicated the metal-fluoro complex hydrolyzed during reaction. A XRD pattern of the product powder is shown in Fig.1. The diffraction pattern showed typical anatase type titanium oxide (PDF #21-1272). Also, thermal analysis showed no exothermic peaks corresponding to recrystallization to anatase TiO_2, which is usually observed around 723 K (Fig. 1(b)). These results indicated that the phase of nanoparticles completely transferred into anatase type structure, although this LPD reaction was carried out under ambient condition.

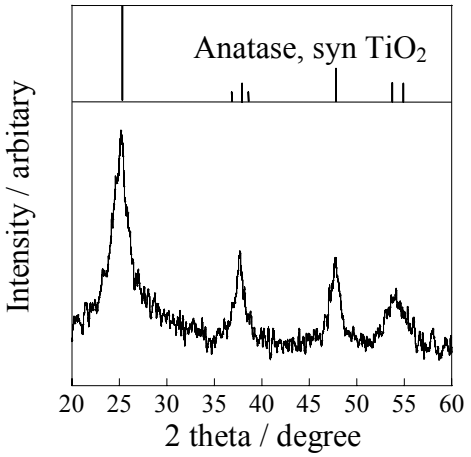

Figure 1 XRD pattern of the synthesized nanoparticles. [PEG200]; 1.1 mol dm^{-3}

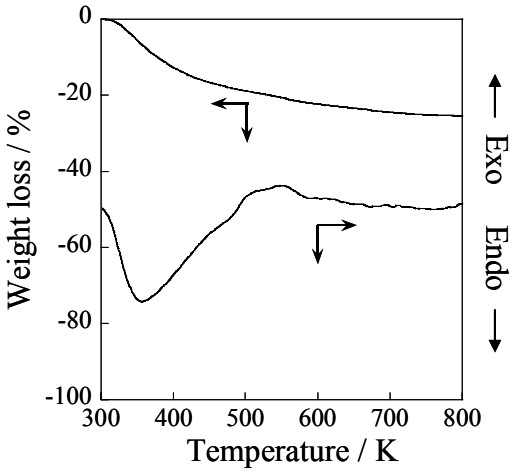

Figure 2 Thermal analysis for the synthesized nanoparticles. [PEG-200]; 1.1 M

Microstructure Analysis

Obtained sample solution was dropped onto carbon supported Cu-mesh for TEM observation. The typical TEM images of nanoparticles obtained by the LPD process are shown in Figure 2a. The image showed that so many nanoparticels uniformly dispersed without any aggregation, whereas it was observed that the TiO_2 have deposited and grown to isotropic direction without PEG as shown in Figure 2b. The diameter of dispersed TiO_2 nanoparticle is *ca.* 3.8 nm and standard deviation is ± 0.4 nm around 10.5 % as shown in Figure 2c (size histograms were obtained by counting ca. 150 particles in the TEM image), which showed the nanoparticles have very sharp size-distribution. In addition, the diffraction ring of anatase type TiO_2 was also confirmed.

In detail observation with high-resolution TEM, we confirmed the lattice fringes for many deposited nanoparticles as shown in Figure 2d. It is observed that some of nanoparticles were similar to single crystal and the interplanar space was approximately consistent with (112) plane of anatase TiO_2. According to the X-ray diffraction (XRD) pattern of the centrifuged nanoparticles, the crystallite size was less than 5 nm in

diameter calculated from the diffraction line width using Scherrer's equation. Particle sizes were determined by TEM observation appeared in general agreement with the XRD determinations.

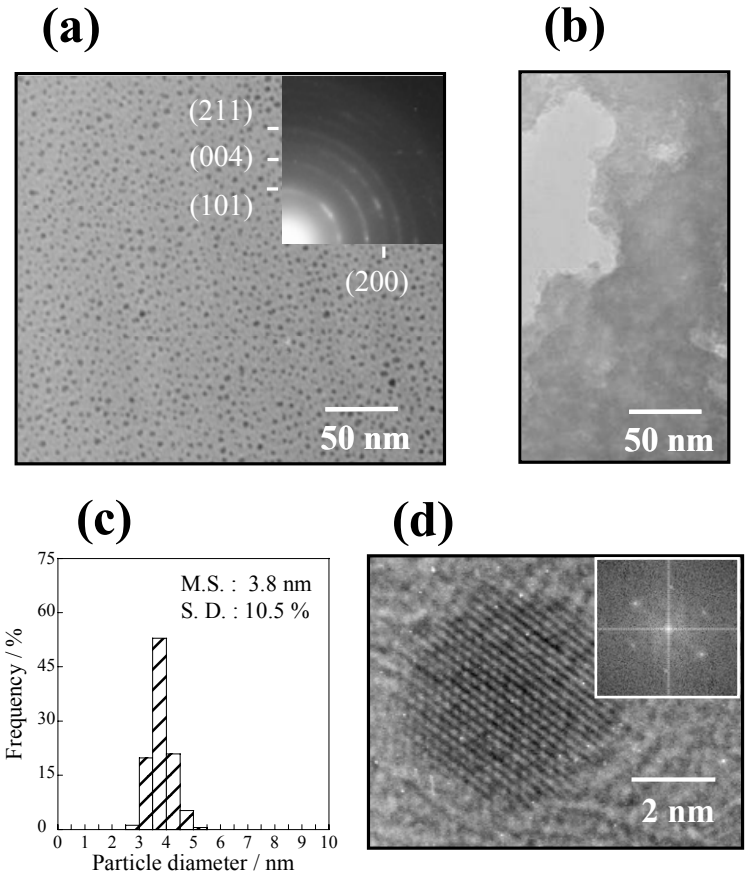

Figure 3 TEM image of (a) the TiO_2 nanoparticles prepared with PEG-200, (b) without the polymer, (c) size distribution and (d) HRTEM images (inset; FFT). [PEG200]; 1.1 M

PEG Concentration Dependence of Particle Size and Yield

Here, PEG concentration dependence on the property of the obtained TiO_2 nanoparticles was discussed. As shown in Figure 4, the increase of PEG concentration leaded the formation of larger anatase crystals. i.e., the particle size distribution could be controlled from 2.8 nm to 5.6 nm of average sizes with PEG concentration. According to previous studies (25), the Raman band in the region of 140 - 160cm^{-1}, so-called E_g band, of anatase phase of TiO_2 shifts with the size of titanium oxide crystallite, due to surface disorder and/or

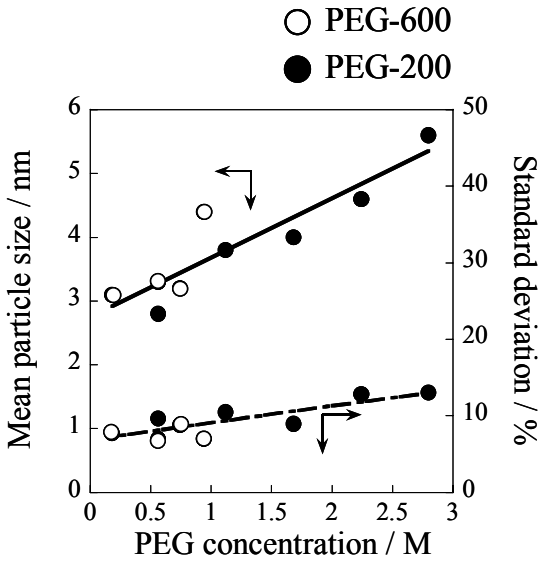

Figure 4 Variation of particle size distribution with PEG concentration.

oxygen vacancy. In the obtained Raman spectra as shown in Figure 5, the band shift due to the average particle size was also observed. Then, it was able to be confirmed with direct and indirect analysis that the particle size could be controlled by the PEG content. The results suggested that the increase of the number of hydroxyl group have reduced the interfacial energy for the titanium oxide to grow up the nanoparticles, because average particle size did not depend on molecular weight, but on the concentration of PEG.

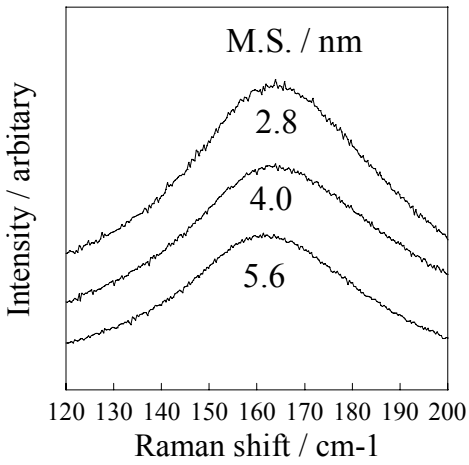

Figure 5 Raman spectra for Eg band of anatase type TiO_2 with various particle size.

Also, the PEG concentration affected the yield of metal-fluoro complex. Here, the yield was defined as conversion ratio of $(NH_4)_2TiF_6$ to TiO_2, that was calculated by dividing TiO_2 content in the obtained particles (calculated from the weight loss at 823K by TG-DTA measurement) by the initial content of $(NH_4)_2TiF_6$ in the treatment solution. The apparent yield of metal-fluoro complex was increased with the PEG content, up to 70% shown as Figure 6a. However, the slope for PEG-600 system was larger than that of PEG-200 system. The difference was attributed to their molecule structure difference, due to the number of ethyleneoxide(EO) units[$-CH_2CH_2O-$], for PEG-200 *ca.*4.1 and for PEG-600 *ca.*13.2. Therefore, PEG-600 has 3 times of EO units compared with that of PEG-200. Then, the relation was normalized with the number of EO unit of PEG-200 and -600. The plot was shown in Figure 6b, which indicate the yield have linearity with EO units. It has been already reported that EO units have a linking structure with $Ti(OEt)_4$ (26). These results suggested that PEG affected the polarity of metal-fluoro complex to increase the reaction rate of hydrolyzing reaction, because of interaction between titanium-fluoro complex and EO units. These results indicated that the number of PEG might have affected the rate of hydrolyzing reaction and growth of titania nanocrystals to thereby determine the particle sizes and size distributions.

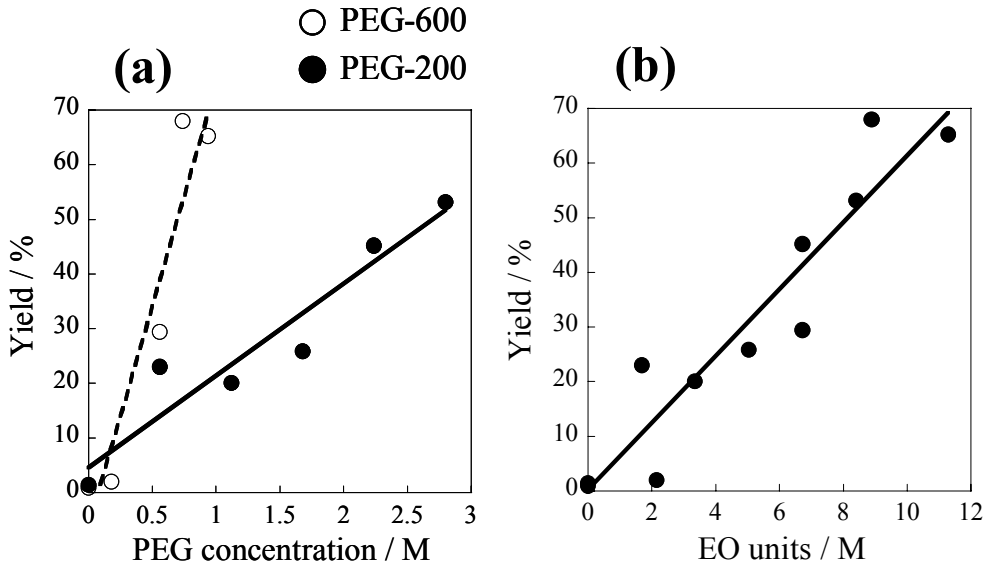

Figure 6 Variation of yield of TiO_2 nanoparticles with (a) PEG concentration and (b) their effective EO units concentration.

Conclusions

Monodispersed TiO_2 nanoparticles was synthesized by the advanced LPD process with controlling the particle size and reactivity of metal-fluoro complex by concentration of aqueous PEG solution in ambient condition.

It is a unique process for preparing pure metal oxide nanoparticles. The particle size could be controlled in the range of ca. 3-5 nm around ca.10% of standard deviation. The crystallite structure of the TiO_2 nanoparticles were assigned to the anatase which formed at ambient temperature with single crystal for each particle.

This novel method represents a very simple route for the preparation of crystalline metal oxide nanopartciles with potentially interesting applications at ambient condition.

Acknowledgements

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