Controlled Crystallization of Ultrafine Titanium Dioxide Particles in the Presence of Hydrophilic or Amphiphilic Polymer from Peroxotitanic Acid

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Controlled crystallization of titanium dioxide ultrafine particles in the presence of water-soluble polymer from peroxotitanic acid was investigated. Heating of aqueous solution of peroxotitanic acid with the polymer at 220 °C for 5 h in an autoclave gave the suspension containing nanometer-sized TiO_2 particles with perfectly controlled crystalline anatase or rutile.

Titanium(IV) dioxide particles are widely used for practical materials in catalysis or photocatalysis, cosmetics, pigments, ceramics, and so on.[1] Chemical properties of TiO_2 particles depend on the crystal polymorphic phases, size, and shape. Therefore, completely controlled preparation of TiO_2 particles is an essential subject in this field. So far, uniform TiO_2 spherical particles were synthesized by hydrolysis of Ti^{4+} and sol–gel process.[2] Especially, it has been receiving great attention that well-controlled preparation of TiO_2 nanometer-sized particles of spindle, cubic, or fiber type, in the reaction systems containing amines or amino acids via sol–gel process was developed by Sugimoto et al.[3] On the other hand, deoxygenation and/or dehydration of peroxotitanic acid, $Ti(OH)_2(OOH)$, which was produced by the oxidation of hydrated TiO_2 sol with H_2O_2, afforded crystalline or non-crystalline TiO_2 particles.[4,5] In these processes, TiO_2 particles should be produced via dehydration of dihydroxytitanium oxide, $TiO(OH)_2$. Thus, the presence of organic compound, being able to coordinate to the oxotitanium species, during dehydration or deoxygenation can be expected to control crystal phase, particle size and shape of TiO_2. This paper describes controlled preparation of rutile or anatase uniform ultrafine TiO_2 particles from peroxotitanic acid in the presence of hydrophilic or amphiphilic polymer.

To a mixture of $1 \, cm^3$ of tetraethyl titanate and $30 \, cm^3$ of ethanol was added $0.5 \, cm^3$ of distilled water and the mixture was stirred for 30 min at a room temperature. Resulting precipitate was centrifugally separated from the solution and dried under reduced pressure. To a $100 \, cm^3$ round flask was added 0.04 g of TiO_2 sol and $50 \, cm^3$ of acetonitrile, and the suspension was irradiated by ultrasonic wave for 1 h. Into the acetonitrile suspension was poured $8 \, cm^3$ of 30% hydrogen peroxide, and then the resulting yellow solution was stirred at 65 °C for 3 h. Polymer was added to the solution and the mixture was agitated at 80 °C for 24 h. After evaporation of acetonitrile, $20 \, cm^3$ of distilled water was added to the past and then the mixture was heated at 220 °C for 5 h in an autoclave. The weight fraction of anatase in titanium oxide was determined by following equation as a function of the strongest reflection, I_A and I_R for anatase(101) and rutile(110) at the Bragg angles 12.68° and 13.73° for Cu Kα radiation, respectively.[6]

$$\text{Fraction of anatase (wt \%)} = 100 \times I_A/(I_A + 1.265 I_R)$$

Transmission electron microscope (TEM) images were observed on Hitachi H-800 with acceleration voltage of 150 kV. Particle size was determined by a dynamic light scattering (DLS) method on an Ohtsuka DLS 7000.

In Table 1, partial results of TiO_2 crystallization in the presence of hydrophilic or amphiphilic polymer are shown. The crystallization with poly(acrylic acid) (PAAc), poly(sodium acrylate) (PAAc-Na^+), poly(methacrylic acid) (PMA), and poly(vinyl alcohol) (PVA) gave anatase-rich TiO_2 particles in the range from 19 to 50 nm, which stably dispersed for long period over 1 week in aqueous solution. Therefore, the reaction with hydrophilic polymer having carboxyl or hydroxyl groups on the side chain led to the formation of nanometer-sized particles. It is also noteworthy that the polymers afforded anatase-rich TiO_2 particles, while amphiphilic polymers of poly(ethylene glycol) (PEG) and poly(ethylene imine) (PEI) gave rutile-rich TiO_2 particles. In most cases, the fraction of anatase or rutile of TiO_2 particles increased with increasing amount of added polymer. At any rate, addition of large amount of hydrophilic polymer resulted in perfect controlling of crystallization. These results, therefore, suggest that coordination of carboxyl or hydroxyl groups on the polymer to peroxotitanic acid or dihydroxytitanium oxide plays an important role in terms of controlling crystal morphs and particle size during crystallization. In

Table 1. Formation of TiO_2 particles in the presence of polymer

Polymer	M_n /10^3	Dosed polymer /mg	Fraction/wt % (anatase/rutile)	Size /nm
PAAc[a]	5	25	100/0	22 ± 2[b]
		100	100/0	18 ± 2[b]
PAAc-Na^{+}[a]	15	25	100/0	140 ± 50[c]
PMA[a]	88	25	67/33	19 ± 2[b]
		50	100/0	17 ± 2[b]
PVA[a]	22	25	90/10	35 ± 4[b]
		100	100/0	50 ± 7[b]
PEG[a]	4	25	3/97	20–700[c]
		100	0/100	20–300[c]
PEI[a]	10	25	17/83	20–800[c]
		100	31/69	20–250[c]

[a]PAAc: poly(acrylic acid), PAAc-Na^+: poly(sodium acrylate), PMA: poly(methacrylic acid), PVA: poly(vinyl alcohol), PEG: poly(ethylene glycol), PEI: poly(ethylene imine). [b]Measured by DLS. [c]Estimated by TEM images.
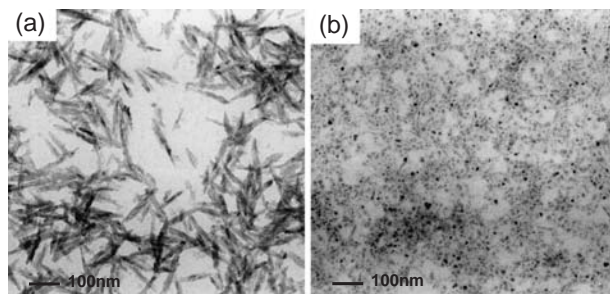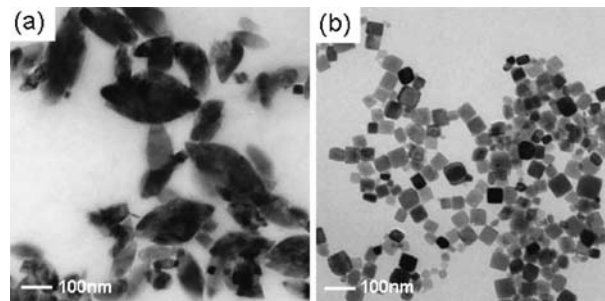
Figure 1. TEM images of TiO$_2$ particles prepared with PMA (a) and PAAc (b).

Figure 2. TEM images of TiO$_2$ particles prepared with PAAc-Na$^+$ (a) and PVA (b) at pH 7.0.

this respect, weak coordination of PEG or PEI to the oxotitanium species due to hydrophobic nature presumably gives large TiO$_2$ particles and stable crystal phase of rutile. Regarding molecular weight of polymer additive, an increase of number average molecular weight of PAAc from 5000 to 25000 scarcely affects particle size and crystal polymorphs of TiO$_2$. It was also confirmed that the crystallization took place with heating at 150 °C, while lowering heating temperature led to increasing amount of amorphous TiO$_2$.

In Figure 1, TEM images of TiO$_2$ particles prepared in the presence of PMA (50 mg) and PAAc (100 mg) were shown. It was observed that fiber-like crystals of 80–100 nm in length and fine particles of 10–20 nm size formed from PMA and PAAc solution, respectively. These results indicated that chemical structure of added polymer dramatically affects shape of TiO$_2$ crystals. Sugimoto et al.[2b,2c] reported the shape of TiO$_2$ particles formed changed with pH in the crystallization via the sol–gel process, i.e., from uniform particles, around 50 nm size, at pH 9.5 to fiber-like crystals at pH 11.6. In present cases, peroxotitanic acid aqueous solution containing PAAc or PMA exhibited pH 4.3, and then the crystallization of TiO$_2$ proceeded under acidic condition. It is therefore suggested that present crystallization was possibly controlled by quite different process from those in the sol–gel method proposed by Sugimoto et al.[2b,2c] In this respect, the reaction system with poly(sodium acrylate) (PAAc-Na$^+$), of average molecular weight 1200, also gave oval-shape particles in the range of size from 50 nm to 200 nm, as shown in Figure 2, similar to TiO$_2$ particles reported by Sugimoto. Peroxotitanic acid aqueous solution containing PAAc-Na$^+$ exhibited pH 5.8. Thus, these results suggested that shape of TiO$_2$ particles was controllable by additive polymer and pH of the solution. The PEG solution gave a mixture of small particles and spindle-type particles of around 200 nm. Probably, weak coordination of PEG to the titanium species induced the formation of thermodynamically stable rutile.

In Figure 2, TEM images of TiO$_2$ particles prepared from PAAc-Na$^+$ and PVA solution at pH 7.0 are shown. PAAc-Na$^+$ solution gave oval-shape crystals mostly the same as those formed at pH 5.8. Interestingly, we could observe relatively homogeneous anatase crystals in hamburger-box shape of 50–80 nm size in PVA solution. Since hydroxyl group of alcohol generally shows a week acidity of p$K_a \approx 18$, the coordination to the oxotitanium species should be much weaker than H$_2$O

molecules (p$K_a \approx 16$). Therefore, complexation of PVA with the titanium oxide species at early stage of crystallization presumably controls their growing to give fine crystalline particles. The reason for the formation of fine crystals in the presence of PVA is yet unclear.

TiO$_2$ particles produced using PMA, PAAc, and PVA stably kept dispersing in aqueous solution over 1 week. Thus, high dispersion of TiO$_2$ particles was probably due to protective colloidal effects of polymer molecules adsorbed on the particles. Indeed, the addition of a poor solvent for coexisting polymer, such as acetonitrile, to TiO$_2$ suspension with PAAc brought about irreversible aggregation of the particles due to precipitation of PAAc to make the polymer on the particle desorbed. In this case, mean particle size of TiO$_2$ particle in the PAAc solution increased to 280 nm from 22 nm after the addition of 6 cm^3 of acetonitrile to the suspension (10 cm^3). Furthermore, successive removal of acetonitrile from the suspension under reduced pressure never returned to the same TiO$_2$ suspension in terms of particle size distribution as the original one.

In conclusion, addition of hydrophilic or amphiphilic polymer controlled crystal polymorphs, size, and shape of TiO$_2$ particles in the crystallization from peroxotitanic acid in aqueous solution. Homogeneous anatase TiO$_2$ particles of hamburger-box or fiber shape in nanometer size could be successively produced.

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