Microwave-Driven Polyol Method for Preparation of TiO_2 Nanocrystallites

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Anatase TiO_2 nanocrystallites have been prepared in 1,4-butanediol, 1,5-pentanediol or 1,6-hexanediol under microwave irradiation by the polyol method. It is demonstrated that the crystallite size less than 10 nm can be controlled by changing the quantity of added water.

Nanosized titanium dioxide (TiO_2) has attracted much attentions for photocatalysts,[1] a dye-sensitized solar cell device[2] and a photonic crystal.[3] The nanosized anatase TiO_2 powder, with a high degree of crystallinity and a monodispersed crystallite size, is regarded important for the enhanced photofunctions. The polyol method was developed over the past two decades and has been applied to the preparation of submicrometer particles such as metal,[4] metal alloy,[5] metal oxide,[6] binary metal oxide,[7] metal sulfide,[8] metal chalcogenide,[9,10] and metal telluride[10] in high boiling point polyol media (e.g., ethylene glycol, diethylene glycol). By using the polyol method, Feldmann et al. recently prepared nanosized TiO_2 particle at 453 K for 2 h in diethylene glycol.[6f]

In recent years, the microwave (MW) technology has been successfully applied to a wide variety of chemical reactions and have consequently been the subject of a number of reviews.[11] Recently, the MW technique has been applied for the first time to the polyol method for the preparation of binary oxide nanoparticles such as $BaTiO_3$, $BaZrO_3$ and $PbTiO_3$ in ethylene glycol because of the high boiling point and the high dielectric loss factor, ε''.[7a] In this paper, we now show the preparation of anatase TiO_2 nanocrystallites in alkanediols ($HO(CH_2)_nOH$, $n = 2$–6) under MW irradiation. This new method enables us to shorten the reaction time and also to control the crystallite size by changing the quantity of water as a reactant.

Microwave irradiation experiments were performed using a microwave apparatus (Micro Denshi MMG-213VP), equipped with a magnetron (2.45 GHz, max. power 1.3 kW), an isolator, a power monitor, a three-stub tuner, a wave guide and a microwave cavity. The reaction temperature was controlled by a thermocouple under the intermittent MW irradiation. The microwave energy was controlled by a power monitor without a loss. The reaction was carried out using a three-neck quartz flask equipped with a water-cooled condenser outside the microwave cavity and the reaction mixture was stirred by a Teflon magnetic stirrer.

Titanium tetraisopropoxide (2 mmol; $Ti(Oi\text{-}Pr)_4$) was added to alkanediol (50 ml) in a 100 ml three-neck quartz flask under nitrogen atmosphere. When 1,5-pentanediol or 1,6-hexanediol was used as a solvent, $Ti(Oi\text{-}Pr)_4$ was not dissolved totally, giving a turbid solution. The solution was irradiated intermittently in the MW cavity at 200 W for 3 min, resulting in rapid rise in temperature to 413 K within 2 min of the irradiation. Then the solution became clear, milli-Q water (1–3 ml) was added, and the solution was irradiated at 900 W. The temperature reached at 513 K within 1 min. Only in the case the quantity of added water was 1 ml, the MW power was reduced to 700 W after the temperature reached at 513 K. This temperature was kept for the remaining irradiation period of 30 min under the intermittent MW 700 W (in the case of 1 ml water) or 900 W (in the case of 2 or 3 ml water). In the case of reaction at 453 K, the MW 200 W was irradiated intermittently for 90 min after 2 ml water was added. At the end of the intermittent MW irradiation, the suspension was cooled down immediately, and diluted with ethanol (30 ml) for quenching further reactions, to yield a precipitate, which was separated by centrifuging at 40000 G for 10 min. The precipitate was twice washed with ethanol under ultrasonication and centrifuged at 40000 G for 10 min, and dried in air.

The products, obtained in 1,4-butanediol, 1,5-pentanediol and 1,6-hexanediol at 513 K for 30 min under MW irradiation, were anatase phase of TiO_2 (Figure 1a–d, powder diffraction file, PDF #21-1272), whereas no anatase formation in 1,2-ethanediol (ethylene glycol) and 1,3-propanediol was recognized by the powder X-ray diffraction (XRD) patterns.[12] At the set temperature, 453 K, it took 90 min for the sample to show the XRD pattern equivalent to that obtained at 513 K for 30 min in 1,5-pentanediol (Figure 1b, 1d). The bright-field transmission electron microscopy (TEM) (Hitachi H-9000) image of the product showed that the anatase TiO_2 nanocrystallites were aggregated (Figure 2a). The 0.35 nm spacing of fringes in the HRTEM image (Figure 2b) corresponded to the *d* value 0.35200 nm of the (101) plane for the anatase TiO_2 (PDF #21-1272). The dark-field TEM image observed for the same areas as in Figure 1a gave a more appropriate image for determining the size distribution (Figure 2c). The distribution determined for the randomly selected 200 particles was centered at 6 nm and ranged between 3 and 10 nm

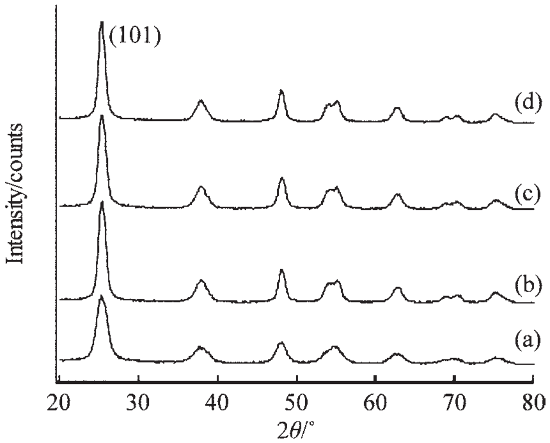

Figure 1. XRD patterns of TiO_2 obtained at 513 K for 30 min (a) in 1,4-butanediol, (b) in 1,5-pentanediol, (c) in 1,6-hexanediol, and (d) at 453 K for 90 min in 1,5-pentanediol under microwave irradiation after 2 ml water was added.

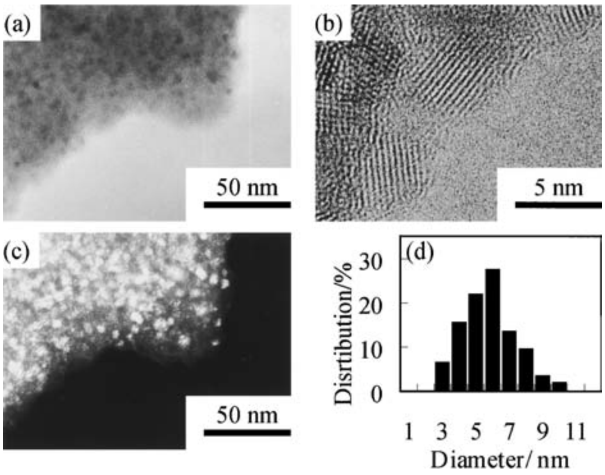

Figure 2. (a) Bright-field TEM image, (b) HRTEM image showing 0.35 nm fringes, (c) dark-field TEM image on the same area in (a), and (d) histogram of size distribution of anatase TiO_2 nanocrystallites prepared in 1,4-butanediol at 513 K for 30 min under microwave irradiation after 1 ml water was added.

(Figure 2d). The average diameter of 5.8 nm was in good agreement with the crystallite size (4.5 nm, Table 1) calculated from the (101) diffraction peak of XRD pattern.[12]

Table 1. Microwave-driven hydrolysis and polycondensation reactions of $Ti(O\textit{i}\text{-}Pr)_4$ (2 mmol) in the presence of H_2O ranging from 1 ml to 3 ml

Solvent	H_2O /ml	Max. Temp/K (Time/min)	Crystallite size of TiO_2/nm[a]
1,2-ethanediol	2	473 (90)	—
1,3-propanediol	2	483 (90)	—
1,4-butanediol	1	513 (30)	4.5
1,4-butanediol	2	513 (30)	5.3
1,4-butanediol	3	513 (30)	6.5
1,5-pentanediol	1	513 (30)	5.9
1,5-pentanediol	2	513 (10)	7.2
1,5-pentanediol	2	513 (20)	8.0
1,5-pentanediol	2	513 (30)	8.3
1,5-pentanediol	2	453 (90)	9.3
1,5-pentanediol	3	513 (30)	10.0
1,6-hexanediol	2	513 (30)	8.1

[a] Calculated from (101) diffraction peak of the anatase phase using the Debye–Sherrer equation.

Using 1,5-pentanediol, the crystallites grew from 7.2 nm to 8.3 nm with the progressing time from 10 min to 30 min (Table 1). The crystallite size prepared in 1,4-butanediol (5.3 nm) was smaller than that in 1,5-pentanediol (8.3 nm) and 1,6-hexanediol (8.1 nm) under the comparable conditions (Table 1). The difference in the chain length of a series of alkanediols led to the precise control of the crystallite size. When the quantity of added water was increased from 1 ml to 3 ml, the crystallite size increased from 4.5 nm to 6.5 nm in 1,4-butanediol, and also increased from 5.9 nm to 10.0 nm in 1,5-pentanediol at 513 K for 30 min under intermittent MW irradiation (Table 1). Therefore, the crystallite size can be controlled by changing the quantity of added water.

In conclusion, we used 1,4-butanediol, 1,5-pentanediol or 1,6-hexanediol as a solvent, and succeeded in preparing size-controlled TiO_2 nanocrystallites by the hydrolysis and polycondensation reactions of $Ti(O\textit{i}\text{-}Pr)_4$ under the intermittent MW irradiation in polyol method. The crystallite sizes rang from 4.5 nm to 10.0 nm only by varying the quantity of water. Selection of the polyols would give broad range of control in the size.

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12 The XRD patterns were recorded using Rigaku MaltiFlex Cu Kα radiation (40 kV, 40 mA) by scanning at 1° (2θ)/min. The crystallite size was calculated from the half-height width of the (101) diffraction peak of anatase phase using the Debye–Scherrer equation: $\lambda = 0.154056$ nm and the shape factor, $K = 0.9$.