Photoactivity and phase stability of ZrO_2-doped anatase-type TiO_2 directly formed as nanometer-sized particles by hydrolysis under hydrothermal conditions

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Abstract

Anatase-type TiO_2 doped with 4.7 and 12.4 mol% ZrO_2 that were directly precipitated as nanometer-sized particles from acidic precursor solutions of $TiOSO_4$ and $Zr(SO_4)_2$ by simultaneous hydrolysis under hydrothermal conditions at 200°C, showed higher photocatalytic activity than pure anatase-type TiO_2 for the decomposition of methylene blue. The crystallite growth and the phase transformation from anatase-type to rutile-type structure caused by heating at high temperature were retarded by doping ZrO_2 into TiO_2. The anatase-type TiO_2 doped with ZrO_2 showed high phase stability and maintained anatase-type structure even after heating at 1000°C for 1 h.
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1. Introduction

Titania (TiO_2) is widely used in various fields of applications because of its interesting and unique properties. Titania is a promising material for photo-electrochemical energy production and has currently received attracted interest as photocatalytic applications for the decomposition of various environmental pollutants in air and in water and solar energy conversion [1–5]. There are several crystal structures for TiO_2: rutile is thermodynamically stable, anatase is metastable, and brookite is formed under hydrothermal conditions [6]. Usually, anatase-type TiO_2 has been selectively used for these photocatalytic applications because of its highest photocatalytic activities. It has been reported that anatase-type TiO_2 changes to rutile-type structure by heat treatment above 635°C from the result of the kinetic study on the transformation from anatase to rutile [7,8], and even with mechanical grinding at room temperature [9]. The polymorphic transformation of

ceramic materials generally depends on the grain size, impurities, composition, nature and amount of the dopant, and so on, which is also governed by precursor materials and formation procedures. The preparation of fine TiO_2 powders and their precursors has been investigated using various methods; vapor decomposition of titanium alkoxides or $TiCl_4$ in oxygen [10], hydrolysis of a dilute alcoholic solution of titanium alkoxides or $TiCl_4$ [11], hydrothermal treatment of a $TiCl_4$ acidic solution [12], hydrolysis of a titanium (IV) sulfate solution [13,14], oxidation of metallic Ti powder [15] and hydrothermal oxidation of metallic Ti powder [16]. We have investigated the direct formation of crystalline nanoparticles of ceramic materials at low temperature through environmental-friendly techniques of soft-solution routes using inorganic metal salts [17–23]. In our previous investigations [24,25], anatase-type TiO_2 synthesized under simple hydrothermal conditions from titanium oxysulfate, $TiOSO_4$, was stable after heating at 800°C for 1 h, and there was no formation of a trace of rutile-type TiO_2, with a high crystallinity and a high photocatalytic activity. We have reported some of the results on finding the occurrence of the direct formation of nanoparticles of CeO_2–ZrO_2 solid solutions by simultaneous hydrolysis of acidic

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aqueous solutions of $ZrOCl_2$ and either Ce(IV) salt [20,21] or Ce(III) salt [26] at 100–240°C. There was a lack of information on the direct formation of ZrO_2-doped TiO_2 with anatase-type structure from acidic aqueous solutions through a similar process. Therefore we have investigated and got the preliminary results on its preparation [27]. The addition of Sb_2O_5, Al_2O_3, ZnO, PO_3^{3-}, SO_4^{2-}, Cl^- [28], SiO_2 [29], phosphate [30], Nb_2O_5 [31], La_2O_3 [32], and ZrO_2 [33, 34] has been shown to retard the anatase–rutile polymorphic transformation. The influences of doping ZrO_2 into the anatase-type TiO_2 on the photocatalytic activity and phase stability of directly formed nanometer-sized particles are interesting to be clarified.

In the present study, ZrO_2-doped TiO_2 having stable anatase-type structure up to 1000°C in air was directly synthesized as nanometer-sized particles from acidic aqueous solutions of $TiOSO_4$ and $Zr(SO_4)_2$ by simultaneous hydrolysis under simple hydrothermal conditions at 200°C and 240°C. The effect of ZrO_2 doping on the photocatalytic activity through the decomposition of methylene blue in aqueous solution, crystallite growth, and phase stability of the anatase-type TiO_2 were investigated.

2. Experimental

2.1. Sample preparation

ZrO_2-doped TiO_2 powders were synthesized under hydrothermal conditions. Reagent-grade $TiOSO_4$ and $Zr(SO_4)_2$ were dissolved in distilled water with total cation concentrations (Ti + Zr) of 0.02, 0.1, and 0.5 mol dm^{-3}. This solution of 18 cm^{-3} was taken into a 25 cm^{-3} Teflon container held in a stainless-steel vessel. After the vessel was tightly sealed, it was heated at 200°C and 240°C for 48 h, under rotation at 1.5 rpm. After hydrothermal treatment, the precipitates were washed with distilled water until the pH value of the rinsed water became 7.0, separated from the solution by ultrafiltration (UK-50, Advantec, Toyo Roshi Co., Ltd., Tokyo, Japan), and dried in an oven at 60°C. The powders thus prepared from the solutions with cation concentration of 0.1 mol dm^{-3} were heated in an alumina crucible, in the temperature range 400–1100°C, for 1 h in air.

2.2. Sample characterization

The phase identification of the as-prepared and heated powders was performed with powder X-ray diffractometry (XRD; model RINT-2000, Rigaku, Tokyo, Japan) using CuKα radiation. The crystallite size of anatase was estimated from line broadening of the 200 diffraction peak, according to the Scherrer

equation. The amounts of rutile phase formed in the heated samples were calculated from the following equation [35]:

$$F_R = 1/\{1 + 0.79[I_A(101)/I_R(110)]\},$$

where F_R is the mass fraction of rutile in the samples, and $I_A(101)$ and $I_R(110)$ the integrated 101 intensities of anatase and 110 of rutile, respectively, both of these lines being around 26° in 2θ. The precipitate morphology and size were examined using transmission electron microscopy (TEM; model JEM-2010, JEOL, Tokyo, Japan). The ZrO_2/TiO_2 molar ratio (mol%) in the samples with single anatase phase was estimated by analysis using an inductively coupled plasma (ICP; model ICP575II, Nippon Jarrell-Ash, Japan) emission spectrometer.

The optical absorption of these prepared powders was measured using an ultraviolet–visible spectrometer (V-560, Nihon Bunko, Tokyo, Japan). Photocatalytic activity of these prepared powders was estimated from the decomposition of methylene blue (guaranteed reagent grade, $C_{16}H_{18}N_3S$, MB), which is often mixed into some fertilizers as a dye. Into an aqueous 2.94×10^{-5} mol dm^{-3} MB solution of 20 cm^{-3}, the sample powders of 0.02 g were added and then irradiated by ultraviolet ray with an intensity of 24 mW cm^{-2} for different periods while stirring. The decomposition rate was estimated from the decrease in the concentration of MB in the solution, which was measured from the absorbance change with a photospectrometer.

3. Results and discussion

3.1. Preparation of ZrO_2-Doped Anatase-Type TiO_2 Powder

Hydrolyses of acidic aqueous solutions of the $TiOSO_4$ and $Zr(SO_4)_2$ were performed under hydrothermal conditions at 240°C for 48 h. Fig. 1 shows XRD patterns of the as-prepared samples (dried at 60°C) directly precipitated from the solutions with a metal concentration of 0.02 mol dm^{-3} at various starting compositions. A precipitate prepared from the composition 100 mol% TiO_2 was a single-phase anatase-type TiO_2. The formation of anatase-type solid solutions doped with ZrO_2 was confirmed by gradual shifting of the 101 diffraction peak of the anatase-type titania to a lower theta angle (in Fig. 1(b)), although precipitation of monoclinic ZrO_2 (in Fig. 1(a)) was simultaneously formed with increasing ZrO_2 content in the starting composition. This result may suggest that the metastable phases bearing large amount of dopants or those having nonstoichiometric compositions are apt to be directly formed under hydrothermal conditions, because similar phenomena were reported in the literature on the direct formation of
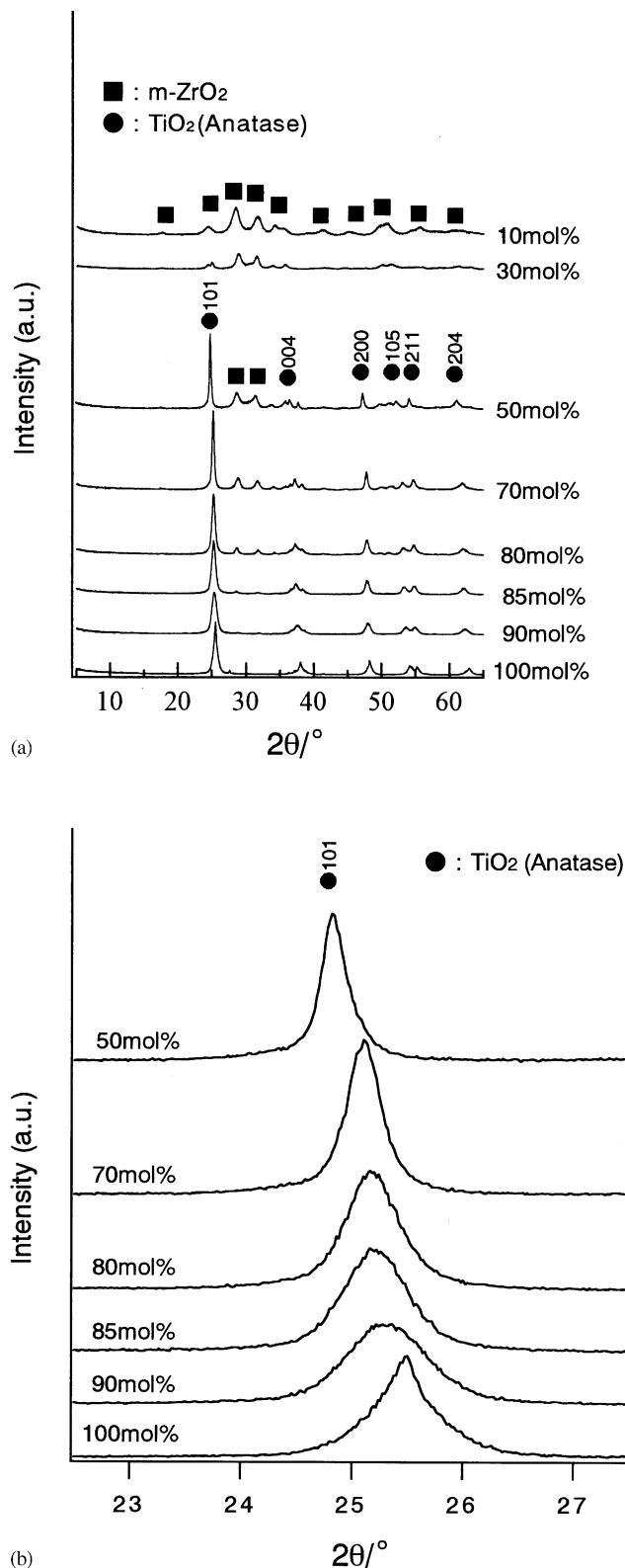
nonstoichiometric $ZnGa_2O_4$ spinel [36] and metastable zircon-type $Zr(Ge,Si)O_4$ solid solutions [37].

XRD patterns of precipitates obtained from the solutions with different cation concentrations are shown in Fig. 2. Monoclinic ZrO_2 phase was not detected in the precipitates prepared from 0.1 and 0.5 mol dm^{-3} solutions as compared with the 0.02 mol dm^{-3} solution at the starting composition of 85 mol% TiO_2:15 mol% ZrO_2. This result implies that the rates of hydrolysis of the $TiOSO_4$ and $Zr(SO_4)_2$ with total cation concentrations of 0.1 and 0.5 mol dm^{-3} well coincide with each other than those with 0.02 mol dm^{-3}.

The analyzed ZrO_2 content in the as-prepared powders that were prepared as a single-phase anatase from 0.1 mol dm^{-3} solution with the starting compositions 90 mol% TiO_2:10 mol% ZrO_2 and 85 mol% TiO_2:15 mol% ZrO_2, is presented in Table 1. The ZrO_2

(a)

(b)

Fig. 1. (a) XRD patterns of precipitates as-prepared from the solutions with cation concentration of 0.02 mol dm^{-3} at various starting compositions from 100 mol% TiO_2 to 10 mol% TiO_2:90 mol% ZrO_2 under hydrothermal condition at 240°C for 48 h and (b) enlargement of the region around 25° 2θ at the starting compositions from 100 mol% TiO_2 to 50 mol% TiO_2:50 mol% ZrO_2.
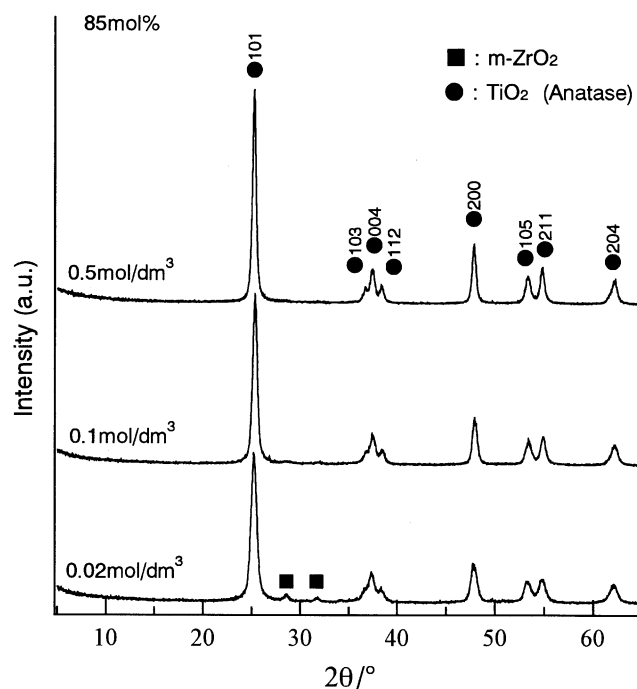

Fig. 2. XRD patterns of precipitates as-prepared from the solutions with cation concentration of 0.02, 0.1, and 0.5 mol dm^{-3} at the starting composition of 85 mol% TiO_2:15 mol% ZrO_2 under hydrothermal condition at 240°C for 48 h.

Table 1
Analytical value of ZrO_2 and optical band gap

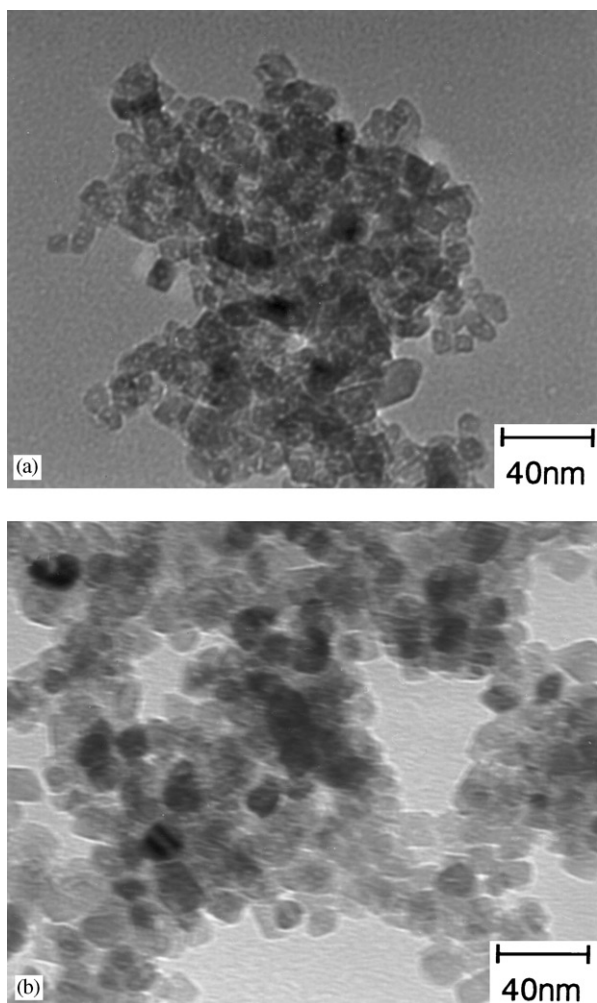| Starting TiO_2 composition (mol%)	Analytical value of ZrO_2 (mol%)	Optical band gap (eV)	
		E_d	E_i
100	—	3.25	2.81
90	4.7	3.28	2.89
85	12.4	3.28	2.91

Fig. 3. TEM micrographs of precipitates as-prepared from $0.1\,mol\,dm^{-3}$ solutions at the starting compositions of (a) 100 mol% TiO_2 and (b) 90 mol% TiO_2:10 mol% ZrO_2 under hydrothermal condition at 240°C for 48 h.

content doped into TiO_2 by the simultaneous hydrolysis of $TiOSO_4$ and $Zr(SO_4)_2$ is found to be less than that of the starting compositions, which is supposed to be due to the difference in hydrolysis rates of the salt solutions between $TiOSO_4$ and $Zr(SO_4)_2$ under the present hydrothermal condition.

TEM micrographs of the as-prepared powders are shown in Fig. 3. The as-prepared anatase-type TiO_2 undoped and doped with ZrO_2, consisted of nanometer-sized particles and the estimation of their crystallite sizes by XRD line broadening method gave 9 and 13 nm, respectively. The particle sizes observed by TEM corresponded well to the crystallite sizes estimated by broadening of the XRD line.

3.2. Phase stability of ZrO_2-doped anatase-type TiO_2 powder

XRD patterns of pure TiO_2 as-prepared and heated at different temperatures for 1 h are shown in Fig. 4(a).
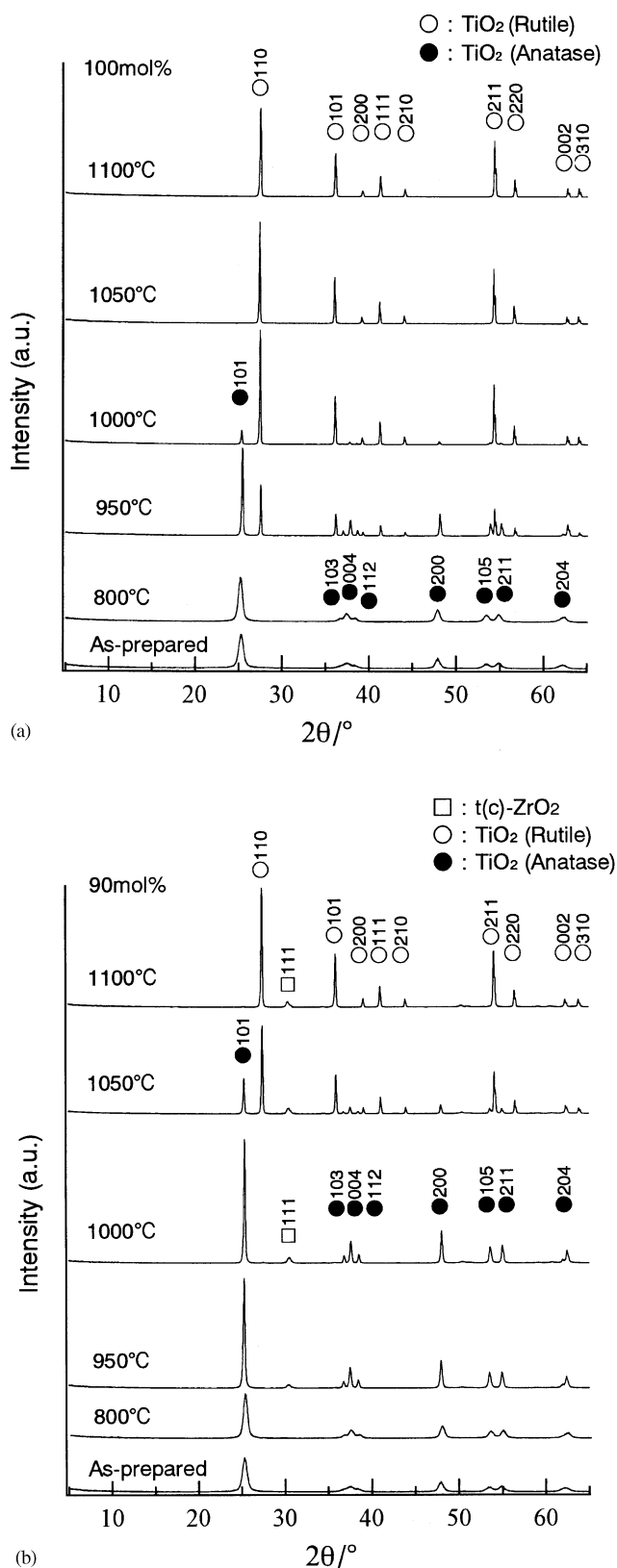

Fig. 4. XRD patterns of the sample powders as-prepared from the solutions with cation concentration of $0.1\,mol\,dm^{-3}$ at the starting compositions of (a) 100 mol% TiO_2 and (b) 90 mol% TiO_2:10 mol% ZrO_2 under hydrothermal condition at 200°C for 48 h and heated in air at different temperatures for 1 h.

The crystalline phase of the as-prepared sample was anatase-type TiO_2 with broad diffraction lines, and no drastic change in diffraction lines before and after heating at 800°C was observed, although three diffraction peaks, i.e., 1 0 3, 0 0 4, and 1 1 2 are separated, which reveals improvement of the crystallinity in the anatase-type structure. No trace of diffraction peaks for the rutile-type structure was detected after heating at 800°C for the pure TiO_2. The sample heated at 950°C clearly showed a partial transformation from the anatase-type to the rutile-type and a single-phase rutile was obtained after heating above 1050°C. Anatase-type TiO_2 powders were reported to easily change into the rutile-type structure by heat treatment at 550–650°C [7,8,38,39]. The transformation temperature from anatase-type to rutile-type for sol-gel-derived TiO_2 powders were also reported to be controlled at the range from approximately 400°C to 700°C by HCl or NH_4OH catalysis addition during the hydrolysis of titanium tetraisopropoxide [40]. For pure TiO_2, stable anatase-type TiO_2 powders have been synthesized by the hydrolysis of the precursor solutions of $TiOSO_4$ and characterized in detail [24,25].

Fig. 4(b) shows XRD patterns of the as-prepared and the heated samples that were formed at the starting composition 90 mol% TiO_2:10 mol% ZrO_2 (analyzed ZrO_2:4.7 mol% (Table 1)). No trace of diffraction peaks for the rutile-type structure was detected for the ZrO_2-doped TiO_2 after heat treatment at 950°C. A small amount of tetragonal ZrO_2 (1 1 1 diffraction line) was detected after heating above 950°C. It is interesting to note that there is hardly any change in crystal phase, and the anatase-type structure is almost maintained even after heat treatment at 1000°C. The ZrO_2-doped TiO_2 thoroughly transformed to a single-phase rutile with a small amount of tetragonal ZrO_2 after heat treatment at 1100°C.

The influence of making solid solutions with ZrO_2 on the crystallite growth of anatase-type TiO_2 during heating has been investigated. The crystallite size of the anatase-type TiO_2 is plotted in Fig. 5 as a function of heat treatment temperature, which reveals that a marked increase in crystallite size for the pure TiO_2 occurs at temperatures above 700°C in comparison with the anatase-type TiO_2 made solid solutions with ZrO_2. The crystallite growth of the anatase-type TiO_2 at temperatures above 800°C is found to be fairly suppressed by doping a small amount of ZrO_2 into TiO_2.

TEM micrographs of the heat-treated samples are shown in Fig. 6. Significant crystallite growth is observed in the pure TiO_2 with increasing heating temperature from 800°C to 950°C (Fig. 6(a) and (b)). With an increase of the amount of ZrO_2 dopant from 0 to 12.4 mol% (analytical composition), suppression of crystallite growth is obviously observed in the TEM
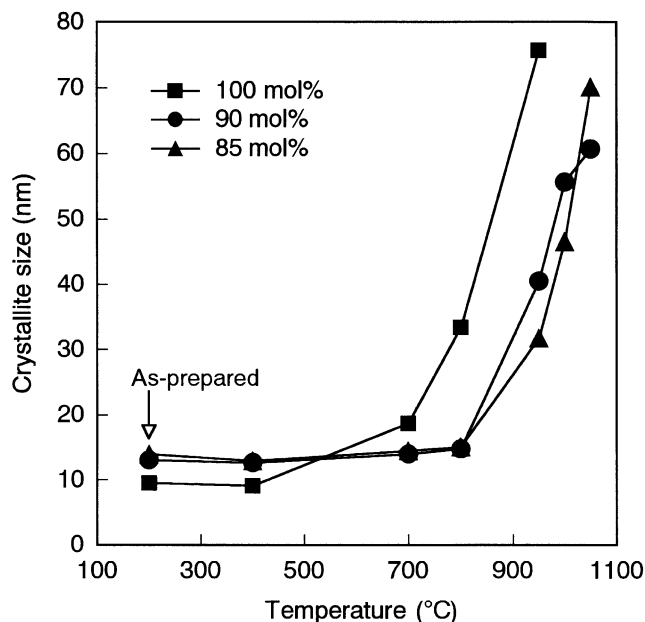

Fig. 5. Crystallite size for anatase powders prepared from the solutions at various starting compositions of TiO_2 plotted against heating temperature.

micrographs. The anatase-type TiO_2 doped with 12.4 mol% ZrO_2, that was heated at 950°C, remained nearly the same crystallite size level as that of the pure TiO_2 heated at 800°C (Fig. 6(a) and (d)), which well agrees with the crystallite size data estimated by XRD line broadening method as shown in Fig. 5.

The effect of making solid solutions with ZrO_2 on the phase stability of the anatase-type TiO_2 is shown in Fig. 7. The rutile-phase fraction (mass%) transformed from the anatase-type structure is plotted for the pure TiO_2 and ZrO_2-doped TiO_2 as a function of heat treatment temperature. It is found that the starting temperature of the transformation from the anatase-type to the rutile-type structure is delayed from 850°C to 1000°C and the phase transformation is almost completed at 1100°C by doping ZrO_2 into TiO_2, although the phase transformation starts at 850°C and completely concludes at 1050°C for the pure TiO_2. These results also reveal that the ZrO_2-doped TiO_2 shows a quick increase in rutile phase concentration, and the phase transformation completes in a short period of temperature range of 100°C in comparison with that of 150°C for the pure TiO_2.

Effectiveness of the addition of Sb_2O_5, Al_2O_3, ZnO, PO^{3-}, SO_4^{2-}, Cl^- [28], SiO_2 [29], phosphate [30], Nb_2O_5 [31], La_2O_3 [32], and ZrO_2 [33,34] for the retardation of the anatase–rutile polymorphic transformation and the acceleration of such a process by the additives of others, such as Fe_2O_3 [41] and CuO were reported. The variation of oxygen vacancy concentration in the anatase structure caused by the presence of foreign ions
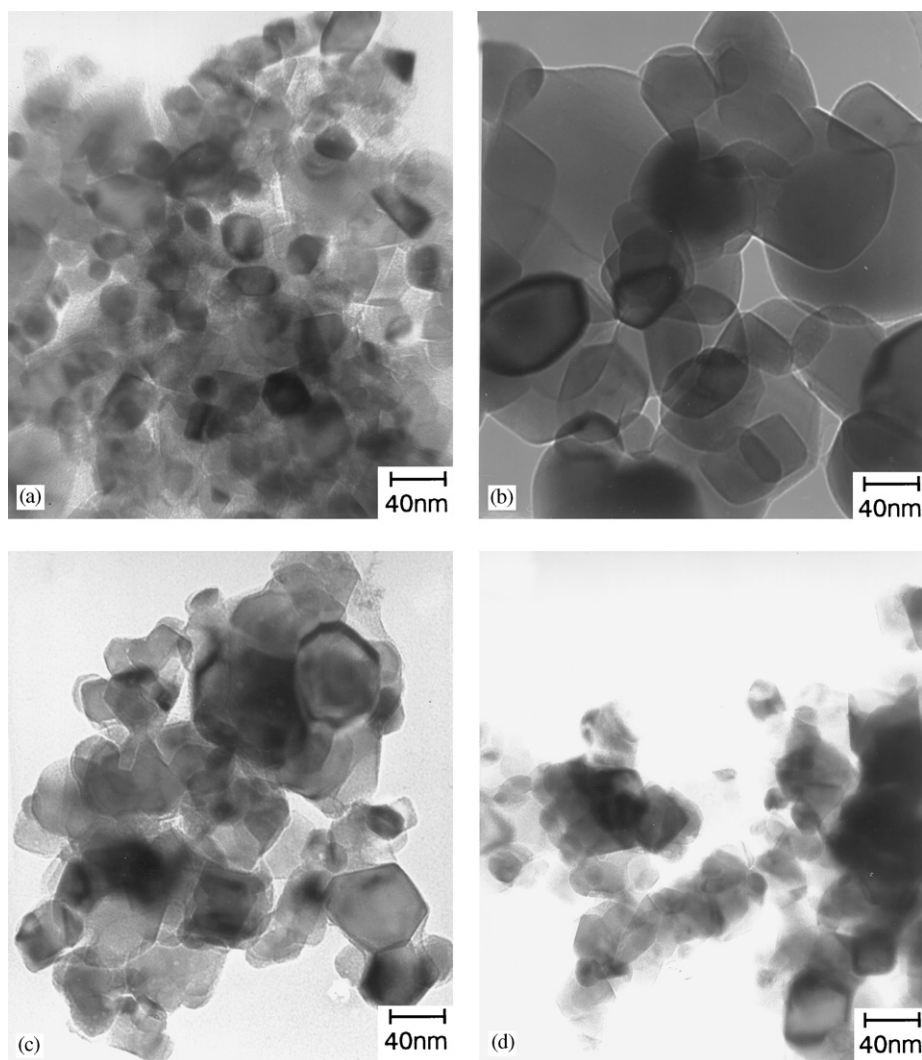
Fig. 6. TEM micrographs of the samples prepared under hydrothermal condition at 200°C for 48 h and heated in air for 1 h: (a) 100 mol% TiO_2 heated at 800°C, (b) 100 mol% TiO_2 heated at 950°C, (c) 90 mol% TiO_2:10 mol% ZrO_2 heated at 950°C, (d) 85 mol% TiO_2 15 mol% ZrO_2 heated at 950°C.

either substitutionally or interstitially was generally proposed to explain the observed accelerating or inhibiting effects [42]. The anatase–rutile phase transformation can occur mostly by thermal activation within an appropriately high temperature range. A metastable anatase phase tends to transform into a more stable rutile phase when the thermal energy is high enough to overcome the nucleation energy, which has been proposed for a similar case of phase transformation from metastable tetragonal ZrO_2 to stable monoclinic one [43,44]. An increase in grain (crystallite) size remarkably and monotonously promoted the transformation during heating near that temperature. The larger-grained microstructure may have had a smaller nucleation barrier for transformation due to the increase in microstructural defects- e.g., dislocations and residual stresses generated locally by the thermal expansion anisotropy within the grain, as insisted in the case of metastable tetragonal ZrO_2 [45,46]. It suggests that increasing grain size decreases the intrinsic phase stability of a metastable anatase grain. In the present study, the anatase–rutile phase transformation is found to occur when the crystallite size reaches approximately 70 nm by heating in both cases for the pure TiO_2 and ZrO_2-doped TiO_2 (which value "70 nm" may be critical crystallite size for transformation estimated by comparing the results shown in Figs. 5 and 7). By doping ZrO_2 into TiO_2, the grain (crystallite) growth is fairly suppressed, which has led to retardation of the phase transformation, because heating at higher temperature is necessary for the ZrO_2-doped anatase-type TiO_2 to reach the critical grain (crystallite) size "70 nm" for the transformation than that in the case of the pure anatase-type TiO_2. In this study, doping ZrO_2 into TiO_2 has
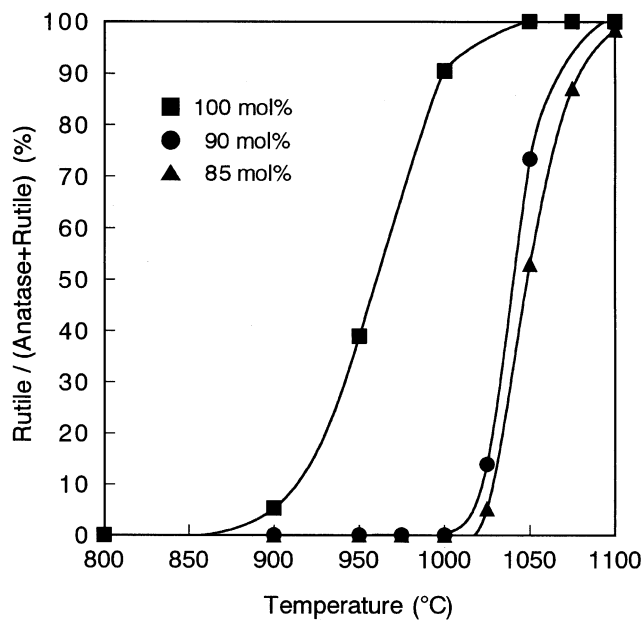
Fig. 7. Phase transformation from anatase-type to rutile-type structure for powders prepared from the solutions at different starting compositions of TiO_2 plotted against heating temperature.
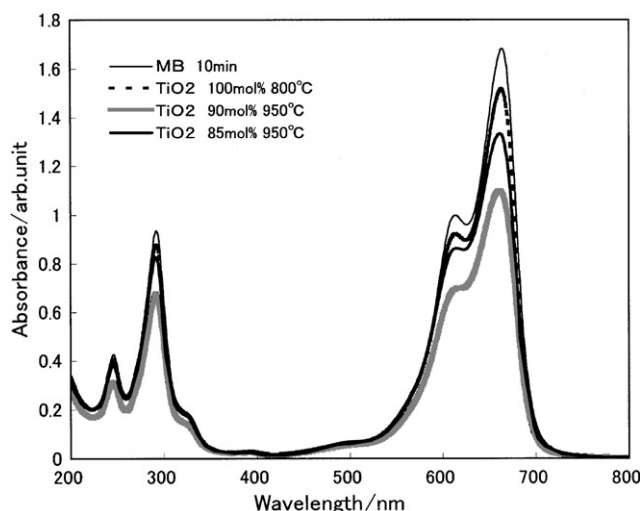

Fig. 8. Absorbance curves after UV irradiation for 10 min for MB solution in the presence of anatase powders prepared from the solutions at the different starting compositions at 200°C for 48 h and heated at different temperatures for 1 h.

been proved to be effective for improving the phase stability of anatase against high-temperature heat treatment.

3.3. Photocatalytic activity

In our previous study [24,25], the crystallinity of anatase-type pure TiO_2 was pointed out to be one of the important factors for the photocatalytic activity by estimation through the decomposition of MB (methylene blue). The ability of MB decomposition for the pure TiO_2 heated at 700°C for 24 h was much superior to that of the as-prepared one [24]. Before the estimation of the photocatalytic activity for the prepared anatase powders, in order to enhance the crystallinity, heating of the pure TiO_2 and the ZrO_2-doped TiO_2 was carried out at 800°C and 950°C for 1 h, respectively. At those temperatures, anatase-type structure of the samples can present satisfactorily stably having high crystallinity and without any trace of detection of diffraction peaks for rutile-type structure on the basis of XRD data after heating as shown in Figs. 4 and 7.

Fig. 8 shows the effect of doping ZrO_2 into TiO_2 on the photocatalytic activity of the anatase-type TiO_2 as the changes in absorbance curve of MB after UV irradiation for 10 min. The pH value of the MB solutions during photoactivity measurement was kept 7. The absorption of the MB by the sample powders without UV irradiation was confirmed to be negligibly small. Therefore, the observed decrease in absorbance of the solution is concluded to be due to the decomposition of MB by photocatalytic reaction of the anatase-type

TiO_2 powders. By doping ZrO_2 into anatase-type TiO_2, the absorption peak around 650 and 250–300 nm decreased their intensity much faster than the case for the undoped pure TiO_2 having higher photocatalytic activity and higher crystallinity than those of the as-prepared one. The 90 mol% TiO_2 (analyzed ZrO_2:4.7 mol%) sample showed the lowest intensity, i.e., the highest decomposition rate of MB. The decomposition ability of MB for the 85 mol% TiO_2 (analyzed ZrO_2:12.4 mol%) sample revealed not to be so marked in comparison with that of the 90 mol% TiO_2 sample, which is considered to be due to an increase in the content of tetragonal ZrO_2 phase appeared separately from the anatase-type structure in the sample powder annealed at 950°C. The excess amount of ZrO_2 having tetragonal phase without making solid solutions with TiO_2 existed in the solid solution sample (85 mol% TiO_2 sample) may shield the photocatalyst from UV light resulting in a poor activity. The crystallite sizes of the pure TiO_2 and ZrO_2-doped TiO_2 used for the estimation of photocatalytic activity ranged from 30 to 40 nm as shown in Fig. 7. The enhancement in photocatalytic activity of the ZrO_2-doped TiO_2 might be explained by the increase of oxygen vacancy concentration according to the mechanism proposed by Yu et al. [47]. Making solid solutions by substituting Zr ions for Ti ions might have some structural defects such as vacancies in its lattice, particularly on the surface to partially offset the lattice strain. Therefore, it is suggested that some oxygen might be escaped from the surface of the lattice to trap the photogenerated holes [47].

In Fig. 9, the changes in absorbance curve with UV irradiation time are shown for the 90 mol% TiO_2 sample
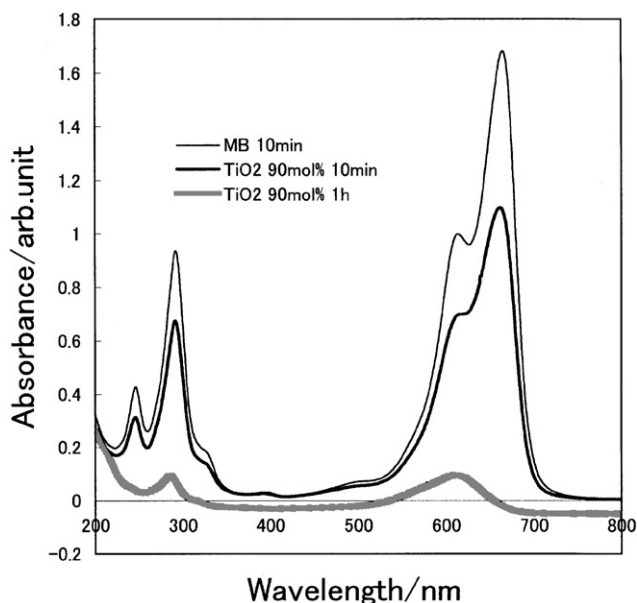
Fig. 9. Changes in absorbance curve of MB solution with irradiation time of UV in the presence of anatase powders prepared from the solutions at the starting composition of 90 mol% TiO_2:10 mol% ZrO_2 under hydrothermal condition at 200°C for 48 h and heated at 950°C for 1 h.
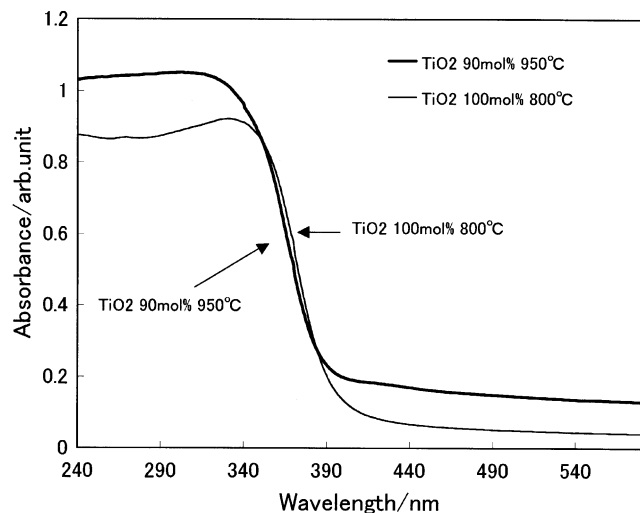

Fig. 10. Diffuse reflectance spectrum of anatase powders prepared from the solutions with different starting compositions of 100 mol% TiO_2 and 90 mol% TiO_2:10 mol% ZrO_2 under hydrothermal condition at 200°C for 48 h and heated at different temperatures for 1 h.

annealed at 950°C for 1 h. The absorbance for MB decreased with increasing UV irradiation time and the MB mostly decomposed after 1 h of UV irradiation.

From the diffuse reflectance spectrum shown in Fig. 10, a slight shifting of the diffuse reflectance spectrum of the ZrO_2-doped TiO_2 to lower wavelength is observed as compared with that of the pure anatase-type TiO_2. It is expected that the optical band gap for

the anatase-type TiO_2 slightly changed by doping ZrO_2. The value of the band gap of the anatase-type TiO_2 and the anatase-type ZrO_2-doped TiO_2 is shown in Table 1, which was determined from the energy intercept by extrapolations of the straight regions of the absorption coefficient $(\alpha h v)^2$ versus photon energy hv for a direct allowed transition (E_d), and the energy intercept determined from a plot of $(\alpha h v)^{1/2}$ versus hv for an indirect allowed transition (E_i). By doping ZrO_2, the value of the band gap is found to become slightly larger than that of the pure anatase, and a slight increase in E_i value has been also confirmed.

4. Summary

Direct precipitation of nanometer-sized particles of anatase-type TiO_2 doped with ZrO_2 was performed by the simultaneous hydrolysis of precursor solutions of $TiOSO_4$ and $Zr(SO_4)_2$ under mild hydrothermal conditions. By doping ZrO_2 into anatase-type structure, the crystallite growth of the anatase-type TiO_2 by annealing at high temperature was apparently retarded and the anatase-type structure was perfectly maintained even after heating at 1000°C. Doping ZrO_2 into the anatase-type TiO_2 was fairly effective for the enhancement of the photocatalytic performance, which was confirmed by estimation through the decomposition of MB.

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