Preparation of titania/silica composite **microspheres** by sol-gel process in reverse suspension

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Abstract

Silica gel **microspheres** were prepared by sol-gel process of silicon tetraethoxide in reverse suspension. **Subsequently,** titanium tetra-2-propoxide solution was added to **the system for producing titania gel**. The composite **microspheres prepared** were

analyzed with optical microscopy, electron probe microanalysis, and X-ray diffraction. **Lowering the titanium alkoxide concentration in the continuous phase was effective to depress the agglomeration of fine titania particles. When the titanium alkoxide solution was divided** into four parts and each aliquot was added separately, **the covering state with titania became most uniform.** The composite **microspheres prepared** were suspended in dye solution under ultraviolet irradiation and examined the possibility of applying to wastewater treatment. **The dye concentration was rapidly decreased more than with a** commercial titania powder, due to the effects of both photodegradation and adsorption.

1. Introduction

Suspension polymerization is one of methods by which polymeric microspheres are prepared. A monomer phase of dispersed phase is poured into an aqueous phase of continuous phase and stirred to form liquid-liquid dispersion. The monomer is polymerized within the dispersed droplet. The final diameter of polymeric spheres

produced directly reflects the droplet size of monomer phase, ranging from a few μm to hundreds μm, which can be controlled by simple operation. Factors influencing the size are stirring strength and its schedule, concentration of suspension stabilizer and its adding method, concentration of initiator, and so on [1−6].

Suspension polymerization is applicable to the preparation of polymer-based composite microspheres, as well as single-phase microsphere [7−13]. It is possible to control the structure by controlling several conditions. These microspheres are used as toner for copying machines and printers and filler for modifying heat conduction.

Silica gel microspheres of tens μm in size are produced by the sol-gel process of silicon alkoxide in reverse suspension [14]. Controlling the initial size of the dispersed droplets can control the final size of silica microspheres. This feature resembles that of suspension polymerization described above. Therefore, it is expected that inorganic composite microspheres with tailored structure can be prepared by applying the techniques of the suspension polymerization. The

purpose of the present study is to confirm this expectation.

The procedure for preparing composite microspheres is much the same as that reported in the previous paper [14]. That is, wet silica gel microspheres were prepared in reverse suspension, and subsequently titanium alkoxide was added into the system to produce titania gel. Characterization of the composite microspheres was done with respect to the content, yield, morphology, distribution, and crystalline phase of titania.

Titania is a photocatalyst, which can oxidize organic compounds in air or water to carbon dioxide and water as well known. The reaction site is the surface of titania. Ultrafine titania powders are used in most studies [15–20], because of the large surface area. However, it is difficult to separate the powder from the suspension after photodegradation processes. To improve this point, titania should be immobilized onto some support. It is thought to be effective to use microspheres of tens μm in diameter as such a support for realizing easy handling with keeping the large surface area. Thus, photodegrading test was done with using the composite microspheres, which were suspended in dye solution as mock wastewater and

irradiated with ultraviolet ray. The photocatalytic activity was compared with that of a commercial titania powder to examine whether they would be useful in cleaning the environment.

2. Experimental

2.1. Raw materials

Silicon tetraethoxide (TEOS) and titanium tetra-2-propoxide (TTIP) were used as alkoxides, sorbitan monooleate (Span80) of oil-soluble surfactant as suspension stabilizer, and hexane as a continuous phase media. Deionized and then distilled water was used as a dispersed phase. pH of the dispersed phase was controlled with acetic acid. Bismarck Brown was used as dye. Commercial titania was used **to compare the** photocatalytic activity. **This powder is composed of 75% anatase and 25% rutile, shown in the catalog.** The grade, purity and manufacturer of these materials are listed in Table 1.

2.2. Preparation

TEOS and Span80 were dissolved in hexane to prepare a continuous phase. TTIP was dissolved in hexane containing Span80 at the same concentration as the continuous phase. A dispersed phase of which pH has adjusted to 1.0 was poured into the continuous phase with stirring at 5.0 s^{-1} to prepare reverse suspension. Flow chart of the procedure is shown in Fig. 1. **TTIP solution of 20 cm^3 at a fixed concentration** was added into the suspension by one of the following three methods:

<Method 1> **The solution of 20 cm^3** was added **all at once** at 24 or 36 h.

<Method 2> The solution was divided into two parts, and each aliquot **of 10 cm^3** was added at 24 and 36 h.

<Method 3> The solution was divided into four parts, and each aliquot **of 5 cm^3** was added at 24, 28, 32, and 36 h.

Stirring was kept for 48 h at 303 K.

Wet gel **microspheres** produced were washed with hexane, ethanol, and methanol in turn and dried at 303 K in atmosphere to obtain dry gel **microspheres**. **They** were calcined for 1 h at 773–1073 K in air with an electric furnace to prepare final composites. The preparation conditions are listed in Table 2.

A preparation tank was a separable flask, inner diameter of 85 mm and capacity of 500 cm^3. Disk turbine-type impeller with 6 blades was used as a stirrer and set at a third of the liquid depth from the bottom. To inhibit the air entrainment from the free surface of the suspension, 4 baffles made of stainless steel were installed.

2.3. Characterization

The morphology was observed with an optical microscope. The signal intensities of characteristic X-ray of TiKα and SiKα were counted with an electron probe microanalyzer (EPMA) for the specimen finely ground. The titania content was determined by comparing the intensity ratio of TiKα/SiKα with that of mixtures of silica produced from TEOS and commercial titania. The distribution of titania was examined **by mapping analysis** with EPMA. **The specific surface area was measured by BET method.** The crystalline phase was identified by powder X-ray diffraction (XRD) with CuKα irradiation.

Photocatalytic activity was tentatively evaluated with using dye solution. Bismarck

Brown aqueous solution at an initial concentration of C_{d0} = 50 g/m^3 was put into four beakers. Commercial titania powder was suspended in two beakers at a concentration of 250 g/m^3. The composite was weighed in order to make the titania content equal to the weight of commercial titania powder and also suspended in the other two beakers. A low-pressure mercury lamp was installed above the beakers, in which the suspensions were stirred with a magnetic stirrer under ultraviolet intensity of 2.5 W/m^2 at the liquid surfaces. The intensity of the absorption spectrum at a wavelength of 460 nm was measured with a spectrophotometer and reduced to dye concentration C_d.

3. Results and discussion

3.1. Titania content

Fig. 2 shows the effect of TTIP concentration C on the titania content X_C of the composites. **When TTIP solution was added by the method 1, X_C increased with the increase in C. The adding time did not affect X_C. At C = 8 mol/m^3, X_C was almost the same, irrespective of the method adding TTIP solution.**

As reported in the previous paper [14], the yield of silica gel microsphere is 80% for 24 h, and 95% for 48 h. That is, most of silica gel has been already produced when TTIP solution was added. TTIP is diffused to the surface or immersed into the inside of the wet silica gel microsphere to hydrolyzed and converted into titania. This process is much faster than conversion of TEOS to silica. It is thought from above results that the formation of titania was terminated within 12 h.

The yield of titania from TTIP was estimated from the results of Fig. **2**. The effect of C on the yield y is shown in Fig. **3**. While y was almost 100% at below 2 mol/m^3, it decreased with the increase in C to 70% at C = 8 mol/m^3. **In this technique, gel is formed from the surface toward the center of the dispersed phase by interdiffusion of the hydrolysis products and H$_2$O through the gel layer having been produced. At higher TTIP concentrations, the interdiffusion is retarded, resulting in the lower yield.**

3.**2**. Morphology

The silica **microspheres** obtained without TTIP were colorless spheres [14]. Fig. **4**

shows the typical optical micrograph of the **wet gel microspheres.** Any change in the appearances was not observed through covering with titania.

Fig. **5** shows the secondary electron image and the characteristic X-ray image of TiKα. **Fine particles of less than a few μm in diameter are observed adhering onto the surface of a silica microsphere of about 60 μm. Such fine particles are not produced in the preparation of silica microspheres. Therefore, they are thought to be titania particles.**

The signal of TiKα is detected not only on fine particles but also on the whole of the composite microsphere. This implies that titania gel covers the surface of silica microsphere. There are areas in which the intensity of TiKα is relatively weak, indicating that the thickness of titania layer is not uniform. The intense signal is detected on a particle of about 10 μm in diameter at the lower place of the figure. This is recognized as an agglomerate of titania.

Fig. **6** shows the **result at** a TTIP adding time of 36 h. **This specimen also does not show uniform distribution of titania.**

A wet silica gel microsphere as substrate has a smooth surface and immerses itself in the dispersed liquid phase. If the sol-gel process of TTIP occurs only at the liquid-liquid interface between the dispersed phase and the continuous phase, resulting composite should have a smooth surface. Therefore, we inferred a mechanism for producing composites as follows.

Alkoxides as raw materials are immiscible with water as catalyst. Therefore, general sol-gel processes are carried out in a homogeneous system by using alcohol as common solvent. Since common solvent is not used in the present study, the system takes the form of reverse suspension that aqueous droplets disperse in nonaqueous continuous phase. TEOS, which is dissolved in the continuous phase, comes into contact with water only at the liquid-liquid interface**.** As a result, spherical silica **microspheres** with preserving the size of the dispersed aqueous droplets are produced. TTIP is added to the continuous phase after a wet silica gel **microsphere** has been formed inside the dispersed phase. Therefore, hydrolysis and dehydration-condensation of TTIP occur at the surface of a silica gel **microsphere** to cover it with titania gel.

Very small amount of water can be dissolved in hexane. It causes the sol-gel reaction of TEOS in the continuous phase. Consequently, **fine** titania gel particles precipitate by homogeneous nucleation **and** agglomerate each other. **Titania agglomerates adhere to a silica gel microsphere, and subsequent heterogeneous nucleation makes the agglomerates grow. Thus, the distribution of titania may become heterogeneous.**

In order to **distribute titania uniformly over the surface of silica microspheres**, formation of the fine titania gel particles in the continuous phase must be avoided. It is necessary for TTIP concentration to be not too high for suppressing homogeneous nucleation. For this reason, dividing addition of TTIP solution was attempted.

Fig. **7** shows the secondary electron image and the characteristic X-ray image of TiKα of the composite **microsphere** prepared by **the** method 2. It is observed that **the distribution of titania is almost uniform**, as expected. This indicates that homogeneous nucleation was suppressed by reducing TTIP concentration in the continuous phase to the half **of the** first addition **of the method 1**. However, production of the titania agglomerates is still recognized, although their amounts were small. Fig. **8** shows the results obtained by the method 3. **The distribution of** titania became more

uniform. The size of agglomerates decreased to below 1 μm.

Table 3 lists the specific surface area of silica and composites prepared at a TTIP concentration of $C = 8$ mol/m^3. Silica calcined at 1073 K reveals surface area smaller than that at 773 K. This may be due to reduction of the pore existing in silica **microspheres** by sintering at higher temperature. The composites calcined at 1073 K are larger in surface area than silica. This **is** attributed to **the existence of** ultrafine titania particles **on the silica microsphere**. Compared by the adding method of TTIP solution, the method 3 provides the smallest surface area. This **result supports** that the decrease in TTIP concentration in the continuous phase has an effect on the depression of homogeneous nucleation.

3.3. Crystalline Phase

XRD was carried out to identify the crystalline phase of the composites, but no diffraction line was detected. This may be responsible for silica being amorphous and titania content below the detectable limit of XRD.

In order to examine the crystalline phase of titania, the same procedure was done without TEOS to prepare titania alone. The diffraction pattern is shown in Fig. 9. Titania calcined at 773 K was single phase of anatase. Rutile content increased with elevating calcining temperature, and it became single phase of rutile at 1073 K. It can be inferred that the same phases were produced also in the composites.

It is well known that **anatase reveals higher photocatalytic activity than rutile. The higher crystallinity it has, the more active it is.** For this purpose, the calcining temperature is desirable to be 773 K, the highest temperature at which single phase of anatase is obtained **in this study**.

3.4. Photocatalytic activity

Fig. 10 shows the change in dye concentration, which is normalized by dividing the dye concentration C_d by the initial concentration C_{d0}. Plots (a) and (b) designate the results when commercial, ultrafine titania powder was used. With UV irradiation (b), the concentration decreased to $C_d/C_{d0} = 0.68$ for t = 180 min. It slightly decreased also without UV irradiation, because of the adsorption of dye molecules onto the surface of

titania particles. Difference between (a) and (b) is considered as net contribution of photocatalytic decomposition by titania.

When the composite calcined at 1073 K was used, reduction of the concentration was more rapid. Even without UV irradiation (c), the concentration outstandingly decreased to $C_d/C_{d0} = 0.38$ for t = 30 min. Thereafter, it gradually decreased to $C_d/C_{d0} = 0.22$ for t = 180 min. **Silica reveals** the specific surface area about ten times as large as 50 m^2/g of the ultrafine titania powder, so that it has more effect of the adsorption. With UV irradiation (d), reduction of the concentration was still steeper. It decreased to $C_d/C_{d0} = 0.16$ for t = 180 min. Much more reduction rate was observed when the composite calcined at 773 K. Difference between (d) and (e) is considered to be due to the crystalline phase of titania produced in the composites, i.e. rutile has been produced at 1073 K, and anatase at 773 K.

4. Conclusions

Adding method of TTIP had a significant effect on the morphology of titania/silica composite microspheres produced. When TTIP was added all at once, the

distribution of titania on the surface of the composites became heterogeneous. By dividing TTIP into four parts and adding at fixed intervals, the formation of ultrafine titania gel particles in the continuous phase was depressed, resulting in the uniform coverage. For degradation of dye solution, the composite microspheres showed performance higher than a commercial titania powder. This was due to adsorption as well as photocatalytic activity. It was confirmed that the sol-gel process in reverse suspension enables the preparation of composite microspheres by simple operation. This method is expected to be applicable to many purposes.

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Table 1

Specification of raw materials

	Grade	Purity (%)	Manufacturer[a]
TEOS	3N	99.9	W
TTIP	Organics	97.0	K
Span80	—	97.5	K
Hexane	Primary	95	W
Acetic acid	Extra	99.7	W
Titania	P25	99.5	A
Bismarck Brown	primary	—	W

[a]W: Wako Pure Chemical Industries Ltd., K: Kanto Chemical Co., Inc.,

A: Nippon Aerosil Co., Ltd.

Table 2

Preparation conditions

Preparation temperature	303 K
Preparation duration	48 h
Stirring speed	5.0 s^{-1}
Volume fraction of dispersed phase	0.050
Concentration of TEOS	0.34 mol/dm^3
Hydrogen ion exponent of dispersed phase, pH	1.0
Concentration of suspension stabilizer	10 mol/m^3
Concentration of TTIP solution C	$1\text{--}8 \text{ mol/m}^3$

Table 3

Specific surface area of silica and composites

Each composite was prepared at C = 8 mol/m^3 and calcined at 1073 K.

Material	Preparation condition	Specific surface area (m^2/g)
Silica	calcined at 773 K	430
	calcined at 1073 K	310
Composite	method 1 at 24 h	700
	method 1 at 36 h	900
	method 2	670
	method 3	470
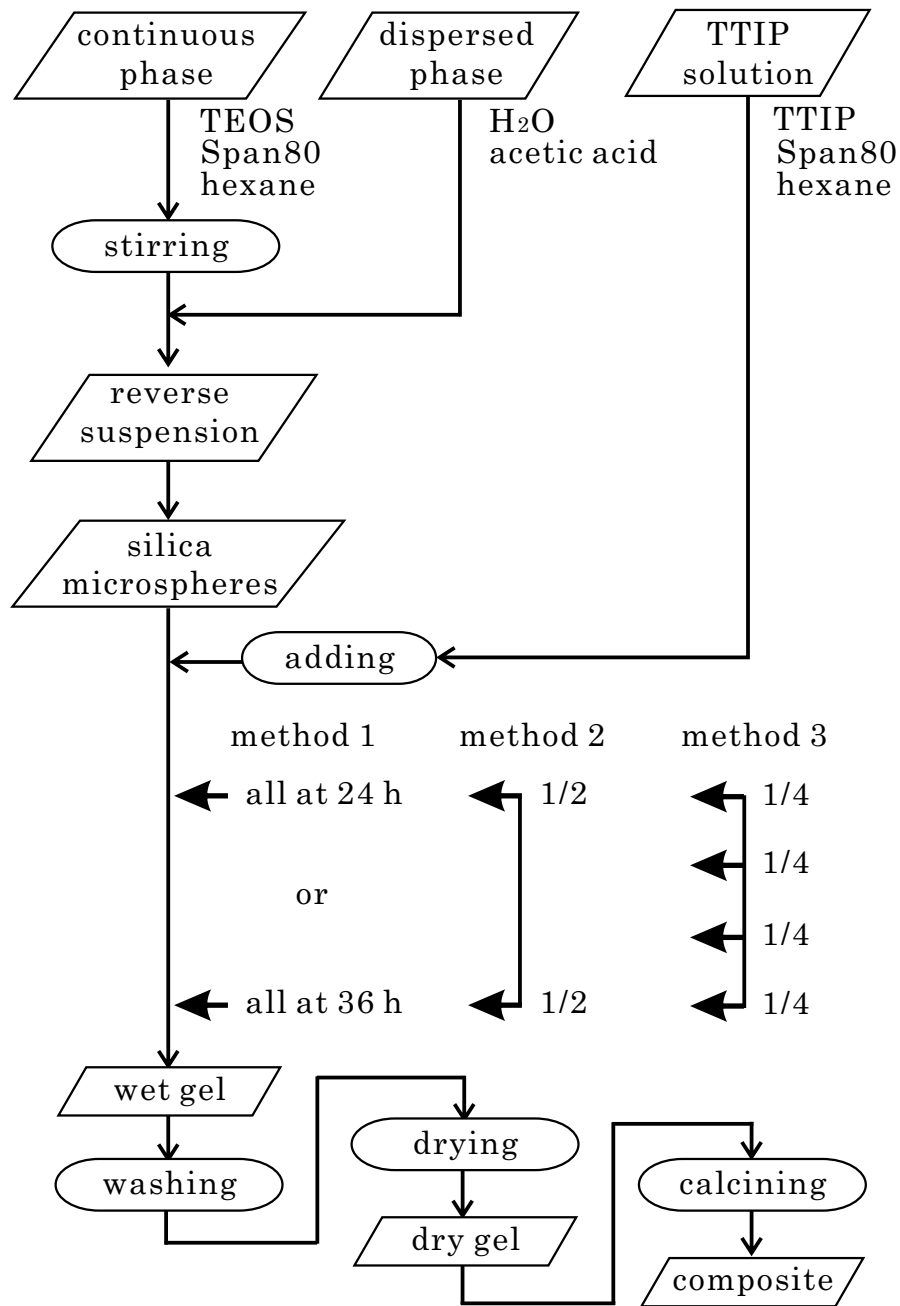
Fig. 1. Flow chart for preparing of composites.
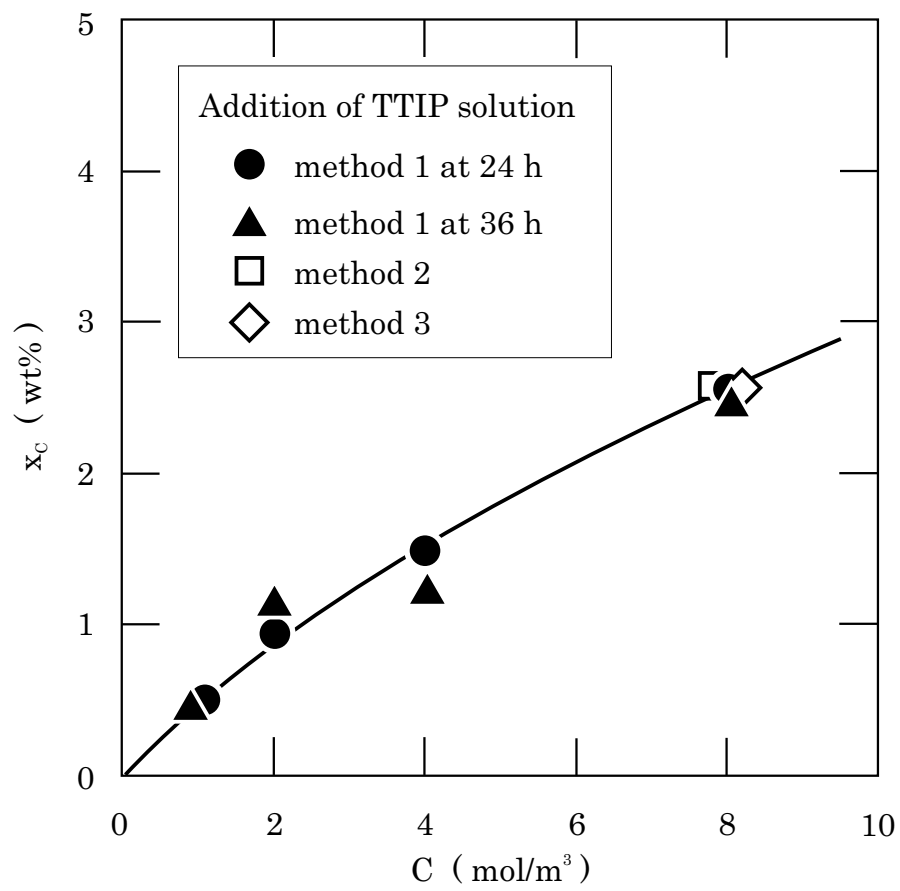
Fig. 2. Effect of TTIP concentration on the titania content of composites.
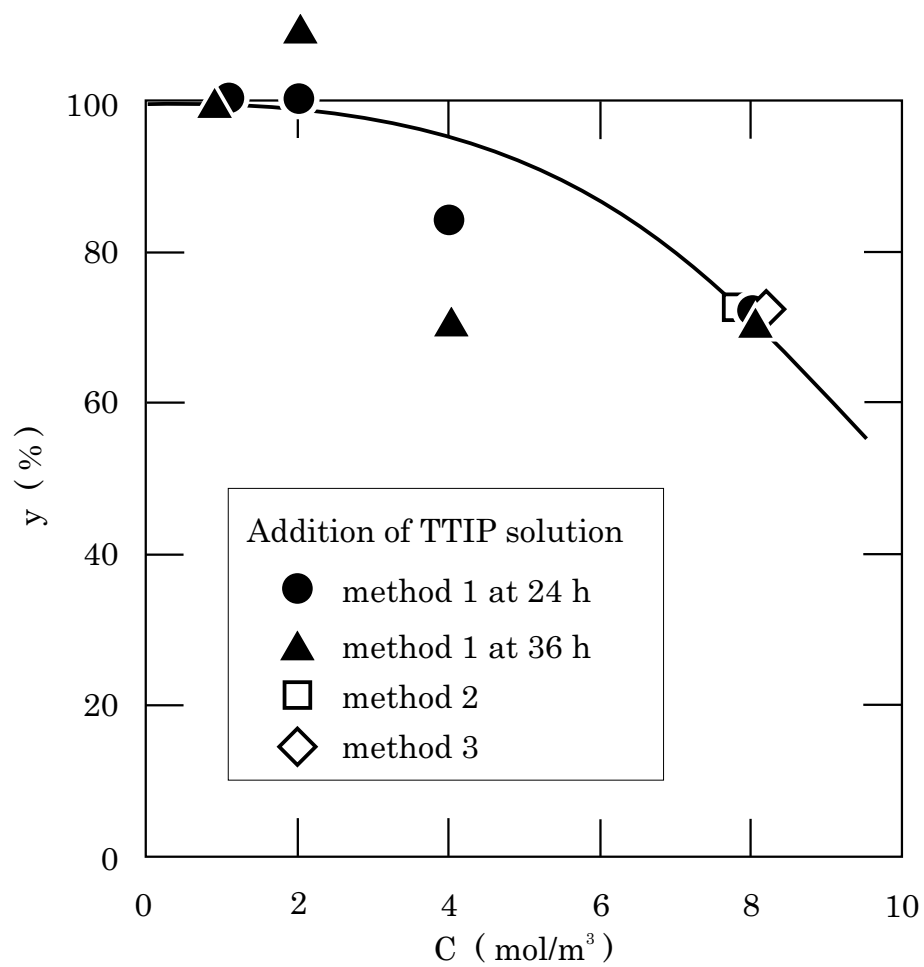
Fig. 3. Effect of TTIP concentration on the yield of titania.
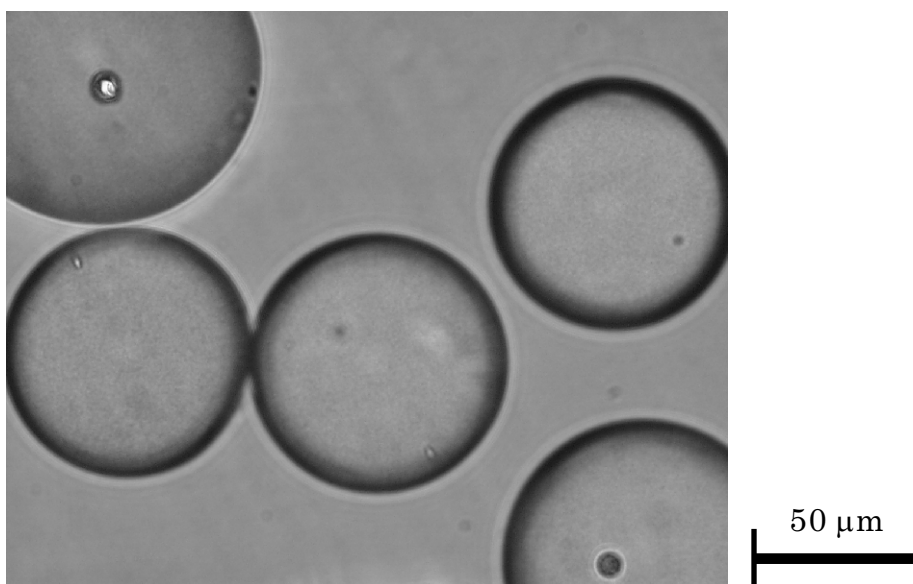
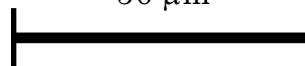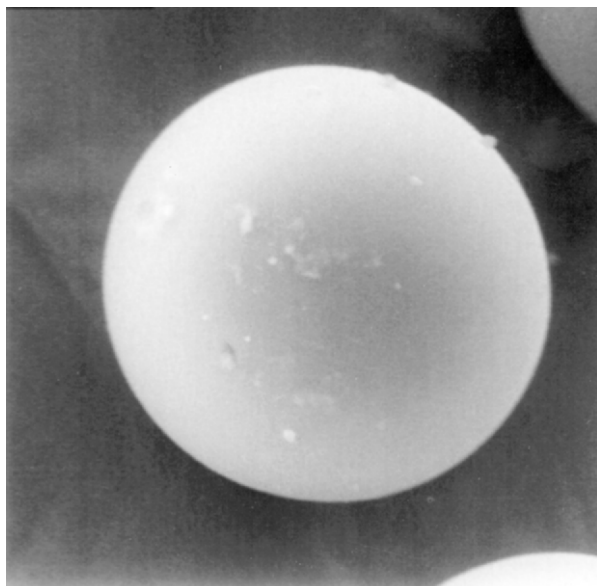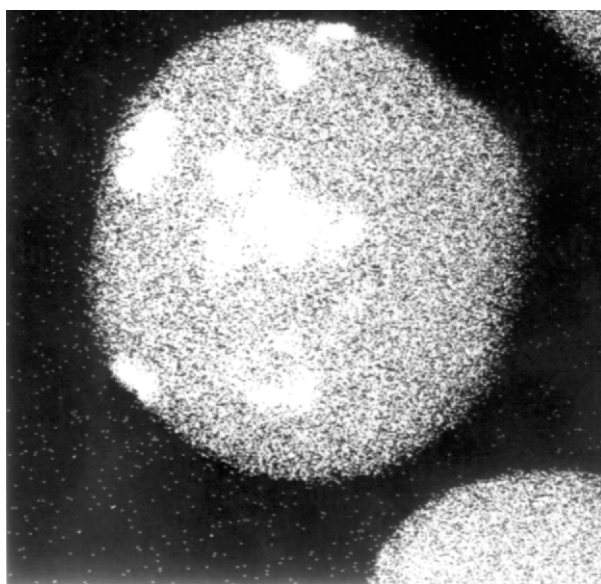Fig. 4. Optical micrograph of wet gel microspheres.

SE

TiKα
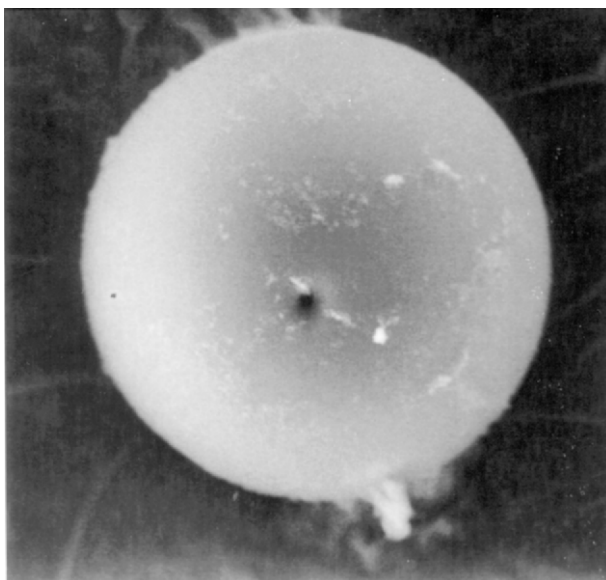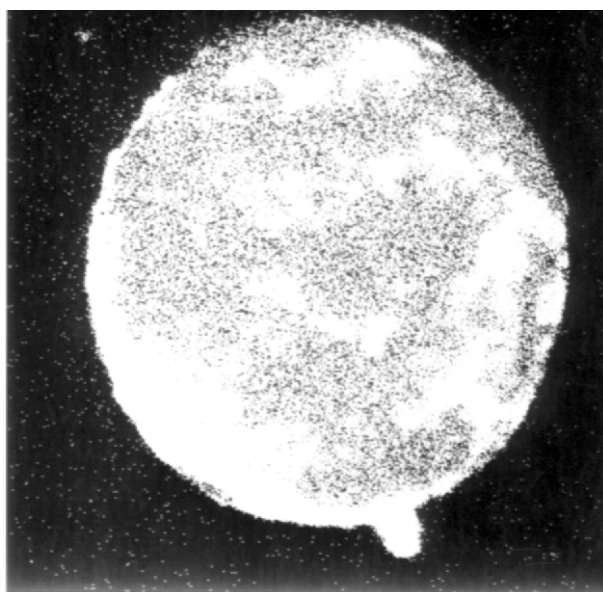
50 μm

Fig. 5. Secondary electron image and characteristic X-ray image of TiKα.
TTIP solution at a concentration of 8 mol/m^3 was added by the method 1 at 24 h.
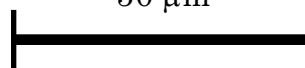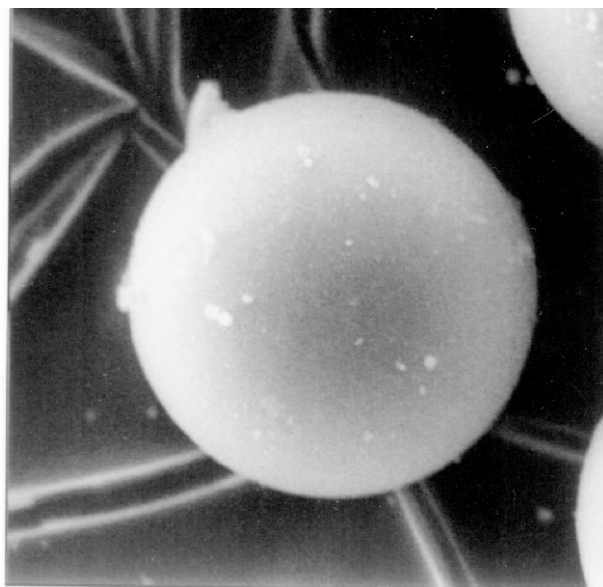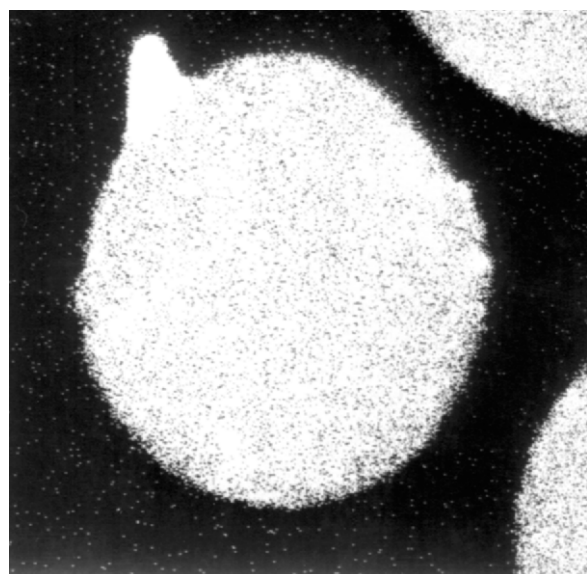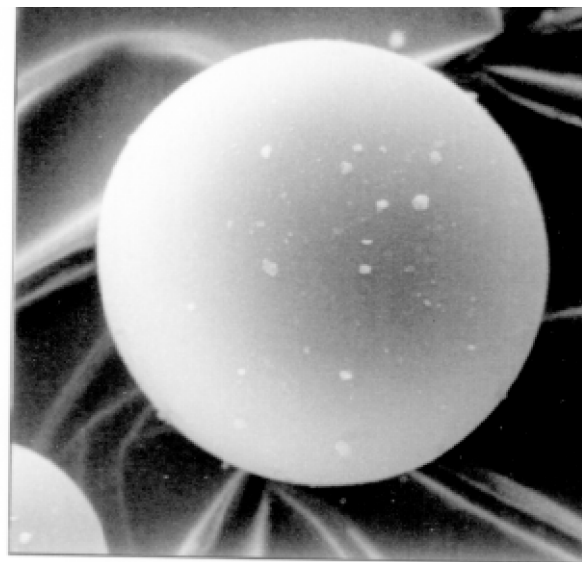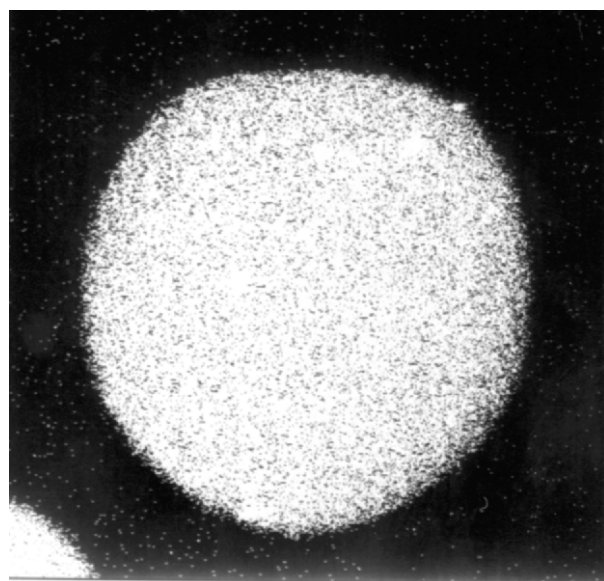
SE

TiKα

50 μm

Fig. 6. Secondary electron image and characteristic X-ray image of TiKα.
TTIP solution at a concentration of 8 mol/m^3 was added by the method 1 at 36 h.

SE

TiKα

50 μm

Fig. 7. Secondary electron image and characteristic X-ray image of TiKα.
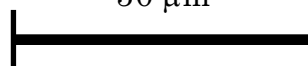TTIP solution at a concentration of 8 mol/m^3 was added by the method 2.

SE

TiKα

50 μm

Fig. 8. Secondary electron image and characteristic X-ray image of TiKα. TTIP solution at a concentration of 8 mol/m^3 was added by the method 3.
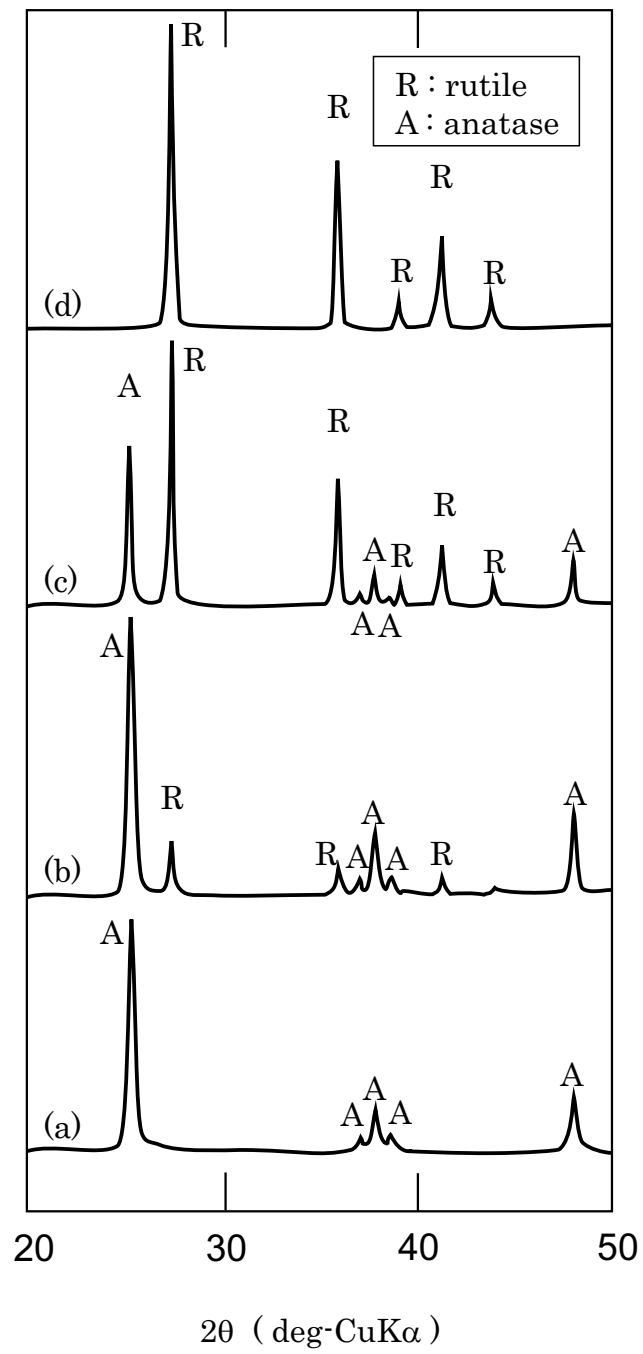
Fig. 9. X-ray diffraction patterns of titania calcined at (a) 773, (b) 873, (c) 973, and (d) 1073 K.
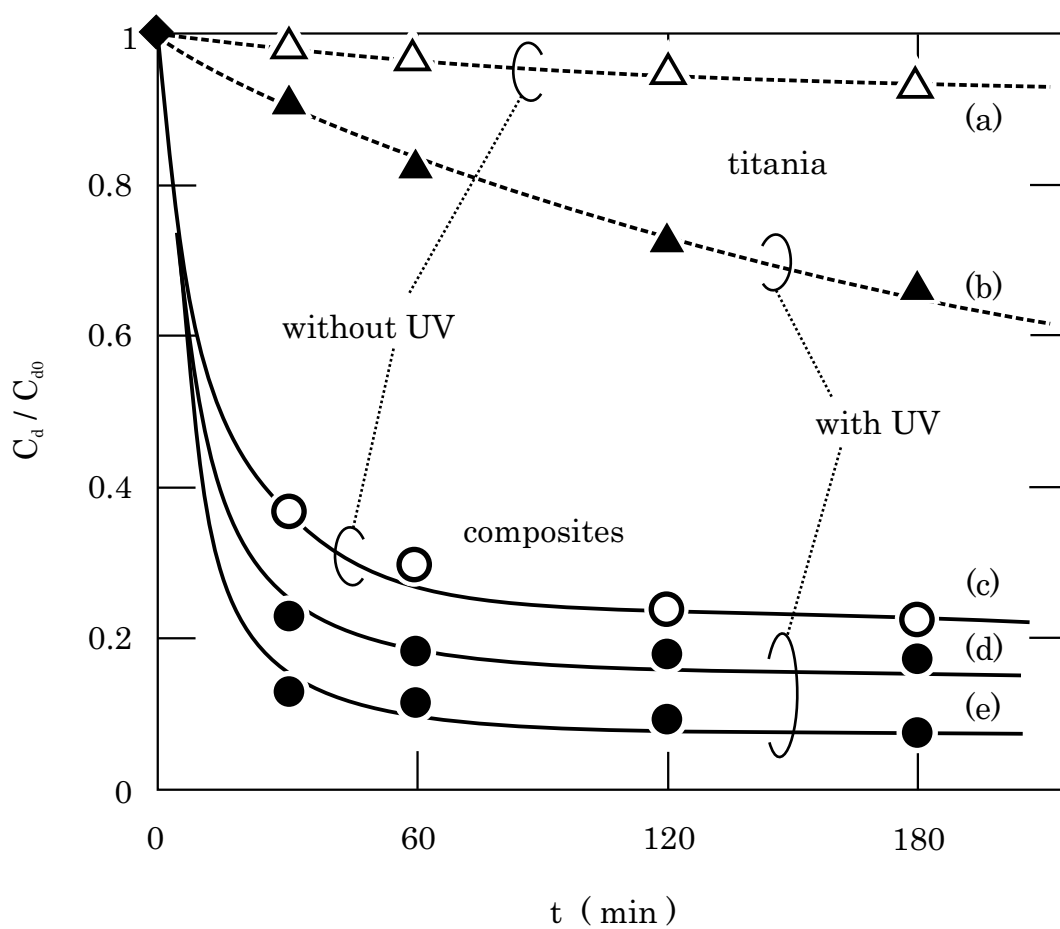
Fig. 10. Photo degradation of dye solution with using (a)(b) commercial titania powder and composites calcined at (c)(d) 1073 K and (e) 773 K.