

The microwave effect on the properties of silica-coated TiO₂ fine particles prepared using sol–gel method

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Received 7 March 2007; received in revised form 15 March 2007; accepted 25 April 2007

Available online 1 May 2007

Abstract

The silica coating of TiO₂ fine particle was conducted using microwave assisted sol–gel method and conventional sol–gel method to suppress its photo-catalytic activity. The amount and uniformity of silica coating on TiO₂ surface were characterized by X-ray photoelectron spectroscopy (XPS), X-ray fluorescence spectroscopy (XRF), infrared spectroscopy (IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and zeta potential measurements. XPS and XRF results showed that the presence of catalyst and reaction time were important factors to reach high silica amounts. SEM, TEM, and zeta potential results indicated that dense film coating of SiO₂ layer formed on TiO₂ surface in conventional sol–gel method, whereas the nucleation coating was observed on sample prepared by microwave assisted sol–gel method. When photo-catalytic activities and ultraviolet (UV) shielding abilities of these samples were evaluated, the sample prepared by microwave processing showed higher inhibition of photo-catalytic activity and better UV shielding ability than the sample prepared by conventional method. These results suggested that the coating method significantly affected the photo-catalytic activity and UV shielding ability of coated TiO₂.

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Keywords: A. Inorganic compounds; B. Sol–gel chemistry; C. Electron microscopy; D. Catalytic properties; D. Surface properties

1. Introduction

Since the intensity of reachable UV-ray increases due to the collapse of ozone layer in past 20 years, the protection of skin from UV-ray has been recently great concerned. Sunscreen agent is one of important tools to protect the skin from UV irradiation. Therefore, the development of effective sunscreen agent is essential in the future [1]. UV filters contained in the sunscreen agent can broadly classified into two categories; organic and inorganic materials. If one compared with organic UV filter, inorganic UV filter is generally accepted as a stable and harmless pigment, and is able to shield wide range of UV-ray [2]. Especially, TiO₂ fine particles (<100 nm) have potential for UV-ray shielding with their absorption, scattering, and reflecting [3] properties which result in widely use of TiO₂ fine particles as UV

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filter [4–6]. Moreover, TiO₂ fine particles also showed high transparency toward visible light making the sealed skin look like natural.

However, it is well known that inorganic UV filter (TiO₂) has the photo-catalytic activity which causes the degradation of organic components contained in sunscreen agent. Therefore, TiO₂ particles (>200 nm) used commercially in cosmetics and paint were coated with inert materials such as Al₂O₃, SiO₂, and ZrO₂ to suppress their photo-catalytic activities [7–10]. TiO₂ fine particles for sunscreens are more active due to large surface area than TiO₂ particles used commercially in cosmetics and paint [7]. Although a large amount of coated inert material require for suppressing the photo-catalytic activity of TiO₂ fine particles, the excess coating would tend to lower UV-ray shielding ability of bare TiO₂ fine particles. Thus, it is difficult for TiO₂ fine particles to suppress its photo-catalytic activity completely while keeping high UV shielding ability. Consequently, controlling the amount and the thickness of coating material is necessary to obtain the coated TiO₂ fine particles with low photo-catalytic activity and high UV shielding ability.

Several researchers had reported the silica-coated TiO₂ fine particles prepared in liquid phase [11–13]. In those studies, anatase-type TiO₂ fine particles (Degussa Co.) were used and anatase-type TiO₂ is well known to possess high photo-catalytic activity [14]. In this point of view, anatase-type TiO₂ was rarely applied for UV-filter contained in sunscreen agent. The UV-ray shielding ability seems to relate with the particle size of TiO₂ [15,16], however, the size of TiO₂ particle is not concerned in those studies. Stamatakis et al. had reported that the range of optimum particle size is 50–100 nm for UVA (320–400 nm) and UVB (280–320 nm) regions [15].

In our previous research [17], conventional sol–gel method (Stöber method) was applied for the control of SiO₂ amounts on TiO₂ fine particles with 80 nm size. It was found that 80% of UV shielding ability and 50% of inhibition extent for photo-catalytic activity toward original TiO₂ fine particles achieved with 5.5 mol% of SiO₂ amount. TEM observation results showed that TiO₂ surface was partially coated with 5.5 mol% of silica, and complete uniformly coating with 2 nm thicknesses was obtained on 22.7 mol% silica-coated TiO₂ fine particles. These results indicated that a large amount of SiO₂ required for complete coating to suppress photo-catalytic activity sufficiently (20% of original TiO₂). Conversely, UV shielding ability significantly decreased from 80% to 55% with an increase in SiO₂ amounts from 5.5 mol% to 22.7 mol%. Therefore, simple increases in SiO₂ amounts limited to inhibit the photo-catalytic activity with keeping high UV shielding ability.

In other previous research [18], a simple, novel and fast technique for silica coating of TiO₂ with poly-diethoxysiloxane (PDES) using microwave irradiation was conducted. The silica-coated TiO₂ fine particles prepared by microwave assisted method showed higher inhibition of photo-catalytic activity and better UV shielding ability than that prepared by conventional method due to a uniform and continuous coating layer on TiO₂ surface. The microwave assisted method excels conventional solution method in a number of advantages such as rapid and homogenous heating, selective heating of desired material and short reaction time [19–22]. We suggested that rapid and homogenous heating makes uniform coating on TiO₂ particles with PDES in only 2 min.

These discussions help us to reach the idea that it is possible to control the size of SiO₂ particles using microwave processing, and then silica-coated TiO₂ fine particles will be formed by combining prepared SiO₂ fine particles with TiO₂ fine particles under microwave irradiation. When TiO₂ surface was densely coated with prepared SiO₂ fine particles, obtained sample will show much higher inhibition of photo-catalytic activity and better UV shielding ability than all products reported in previous researches.

Thus, in present study, silica-coated TiO₂ fine particles were prepared using microwave apparatus in liquid phase *via* sol–gel reaction between TEOS and commercial rutile-type TiO₂ powder (Ishihara Co.; TTO-V3). Additionally, SiO₂ coating was also carried out by conventional sol–gel method and the properties of silica-coated TiO₂ fine particles were compared, and then the effect of microwave on the property of prepared sample is discussed.

2. Experimental

2.1. Materials

TiO₂ fine particles (Ishihara Co., TTO-V3, rutile-type, 150 m² g⁻¹) were used as starting material. This is previously modified with Al₂O₃, and is commercially used as a UV-filter. It was confirmed from XRF measurement result that 5 mol% of Al₂O₃ contained in TTO-V3 sample. Tetraethoxysilane [TEOS: Si(OC₂H₅)₄, 95%] was purchased from KANTO CHEM. Co. Inc.. NH₃ aqueous solution (pH 12) were prepared by the dilution of NH₃ aq. (Wako Pure Chem. Ind. Ltd., 25 wt.%). This solution was used as a catalyst.

2.2. Sample preparation

Silica-coated TiO₂ fine particles were obtained *via* sol–gel reaction. Microwave assisted sol–gel method and conventional sol–gel method in liquid phase were conducted in present study.

2.2.1. Microwave assisted sol–gel method

Ethanol (70 ml)–TiO₂ (2 g) dispersion and water (30 ml)–TEOS (2 g) solution was mixed with and without the addition of catalyst (pH 12) in glass vessel. Glass vessel was set inside the microwave apparatus (Shikoku-keisoku, SMW-064, maximum power 500 W, 2.45 GHz) and mixture was started to be stirring by magnetic stirrer. Then, the mixture was heated up to 343 K with a heating rate of 1 K s⁻¹, held at 343 K for 2 min and cooled down to room temperature. After slurry product was collected using centrifugation apparatus (3000 rpm, 20 min), the material was obtained by washing with ethanol repeatedly and drying at 353 K for 6 h in a vacuum oven.

2.2.2. Conventional sol–gel method

Firstly, TiO₂ dispersion and TEOS solution were prepared separately. After grinding of TiO₂ agglomerates with ethanol in planetary ball mill (370 rpm, 5 min), ethanol–TiO₂ dispersion was prepared by stirring strongly in ethanol with and without the addition of catalyst (pH 12). TEOS–ethanol solution was prepared by mixing of TEOS and ethanol. The weight ratio R' (=TEOS [g]/TiO₂ [g]) was adjusted to 1. Sol–gel reaction was started when TEOS solution was added to TiO₂ dispersion, and then the mixture was stirred for 6 h at room temperature. After slurry product was collected using centrifugation apparatus (3000 rpm, 20 min), the material was obtained by washing with ethanol repeatedly and drying at 353 K for 6 h in a vacuum oven.

2.3. Sample characterization

The nitrogen adsorption isotherms of samples (0.1 g) were measured using a SA3100 (Beckman Coulter Co.) to calculate the specific surface area based on the BET method.

The chemical compositions of samples were determined by X-ray fluorescence spectroscopy (XRF) using SEA2010 (SEICO Instruments Inc.) and calculate the amounts of Si (%) using Eq. (1) described below:

$$\text{Si amount (\%)} = \frac{\text{Si (mol\%)}}{\text{Si (mol\%) + Ti (mol\%)}} \times 100 (\%) \quad (1)$$

XPS measurements of silica-coated TiO₂ particles were performed on a Physical Electronics ESCA 5600ci spectrometer with a monochromatic Al K α X-ray source at a power of 300 W. The XPS spectra used in this study were survey spectra (pass energy of 187.85 eV) of samples and the emission angle from the surface normal for the spectra used here was 45°. The amounts of Si (%) were also calculated using the following equation:

$$\text{Si amount (\%)} = \frac{\text{Si (atom\%)}}{\text{Si (atom\%) + Ti (atom\%)}} \times 100 (\%) \quad (2)$$

The infrared spectra of non-coated and coated TiO₂ were measured using a FT-IR spectrometer (FT/IR-430, Jasco) to observe the surface functional groups of samples, especially ethoxy and hydroxyl groups.

XRD measurements of non-coated and coated TiO₂ were performed on a Rigaku powder diffractometer with Cu K α radiation. The tube voltage was 40 kV, and the current was 40 mA. The XRD diffraction patterns were taken in the 2 θ range of 20–60° at a scan speed of 2° min⁻¹.

The sizes of silica-coated TiO₂ particles were measured by particle size distribution analyzer (Zeta pals, Brookhaven Instruments Inc.) with Dynamic Laser Scattering mode (DLS). Firstly, prepared silica-coated TiO₂ particles were dispersed with ethanol and the solution treated under supersonic wave prior to measurement was introduced in glass cell. Then, the measurements were conducted and the results were collected. Zeta potential measurements of non-coated and coated TiO₂ particles were conducted using Zeta pals (Brookhaven Instruments Inc.). A 0.02 g of powder was mixed with 100 ml of distilled water and the mixture was treated under supersonic wave for 30 min. The pH values were adjusted by the addition of 0.1 M HCl or 0.1 M NaOH aqueous solutions.

The size and morphology of silica-coated TiO₂ particles prepared by conventional sol–gel method and microwave assisted sol–gel method were observed by scanning electron microscopy (SEM: Hitachi S-4500) and transmission electron microscopy (TEM: Hitachi H-7650) to investigate the effect of preparation method on particle size and morphology of coated TiO₂ particles.

2.4. Estimation of photo-catalytic activity

The photo-catalytic activities of non-coated and coated TiO₂ particles were evaluated using 1,3-butanediol (1,3-BG; purity > 98.0%, purchased from Kanto Chem. Co. Inc.) method. Firstly, the paste of TiO₂ and 1,3-BG (weight ratio 4:3) was prepared by physical mixing, and the mixture was placed between glass plates. Then, UV light (Max 352 nm, 0.19 W/cm²) was irradiated to sample for 1 h. Exposure of the paste with UV irradiation causes the photo-reduction of TiO₂ to lower oxide and the color of the paste changes from white to blue [23]. The color difference (ΔE) between the sample before UV irradiation and the sample after UV irradiation was measured by color spectrometer (NF333, NIPPON DENSYOKU) with L*a*b* color system. The relative photo-catalytic activities of TiO₂ particles were calculated by using the following equation:

$$\text{photo-catalytic activity} = \frac{\Delta E^S}{\Delta E^0} \times 100 (\%) \quad (3)$$

where ΔE^S : ΔE on silica-coated TiO₂ particle, ΔE^0 : ΔE on TiO₂ particle.

2.5. Evaluation of UV shielding ability

UV–vis measurements were performed for evaluating the UV shielding ability. A 0.1 g of sample powder, 0.15 g of liquid paraffin oil and 10 ml of nitrocellulose were mixed uniformly using planetary ball mill with 40 g of zirconia ball at 370 rpm for 10 min. The dispersion mixture was then applied to polypropylene film with a box applicator and measured by UV–vis spectrometer (Jasco Co., V-560). The UV shielding ability was calculated by using the following equation:

$$\text{UV shielding ability} = \frac{B}{A} \times 100 (\%) \quad (4)$$

where A and B in equation are the areas calculated by integrating transparency difference from base line, which is defined as value at 700 nm, in the range of 280–350 nm wave number. Then, A is UV shielding ability of original TiO₂ particles, and B is that of coated TiO₂ particles.

3. Results and discussion

3.1. Characterization for prepared silica-coated TiO₂ particles

Table 1 summarizes the characterization results for silica-coated TiO₂ particles prepared by microwave assisted sol–gel method and conventional sol–gel method. In present study, the preparation conditions represent as (A) microwave assisted sol–gel method without catalyst, (B) microwave assisted sol–gel method with the catalyst of NH₃ aqueous solution (pH 12), (C) conventional sol–gel method conducted for 6 h without catalyst, and (D) conventional

Table 1

The characterization results for silica-coated TiO₂ particles prepared by microwave assisted sol–gel method and conventional sol–gel method

Sample number	Method	Catalyst	BET surface area (m ² /g)	Si amount (%) (XRF)	Si amount (%) (XPS)
A	Microwave assisted sol–gel	No	124	1.4	9.0
B		pH 12	106	14.8	59.9
C	Conventional sol–gel	No	141	1.6	6.3
D		pH 12	93	21.4	72.0

sol–gel method conducted for 6 h with the catalyst of NH_3 aqueous solution (pH 12). It can be seen that the BET surface area of all coated samples was decreased from one ($150 \text{ m}^2 \text{ g}^{-1}$) of original TiO_2 fine particles. The results of XRF measurements showed the existence of Si atoms over all coated samples. Furthermore, obtained Si amounts of all coated samples from XPS analyses were much higher than Si amounts estimated from XRF results (Table 1). This implies that coating material was deposited on TiO_2 fine particle surface. The different contents of Si on the samples attribute to different preparation conditions. Large extent of decrease in surface area and highest content of Si were observed on the sample prepared under (D) condition which indicates that the presence of catalyst and reaction time are important factors to reach high SiO_2 amount. Although the reaction time was only 2 min, the sample prepared under (B) condition showed the relative high content of Si. This phenomenon can attribute to higher reaction temperature (343 K) and different heating mechanism.

Fig. 1 shows the FT-IR spectra of original TiO_2 particles and coated TiO_2 particles prepared by microwave assisted sol–gel method without catalyst (Fig. 1(b)) and with catalyst (Fig. 1(c)). All spectra showed that there were a large amount of water and hydroxyl groups existed in all samples because of the presence of a bending vibration of H–O–H at 1630 cm^{-1} , and a strong stretching vibration of O–H at 3400 cm^{-1} [24–26]. The band at $800\text{--}400 \text{ cm}^{-1}$ assigned to Ti–O–Ti was observed over all samples. Additionally, the band at 1040 cm^{-1} assigned to the asymmetric stretching vibration modes of the Si–O–Si bridge of the siloxane link [11–13,26] was observed over coated samples (Fig. 1(b) and (c)), however, the band at 965 cm^{-1} corresponding to Si–O–Ti [11–13,26] was not observed clearly due to overlapping with the band at 1040 cm^{-1} . These observations indicate that the direct bonding between Ti atom of TiO_2 and Si atom *via* O atom were not confirmed by FT-IR measurements. Moreover, the band at around 1400 cm^{-1} assigned to the deformation vibration of CH_3 groups or CH_2 groups [25,27] was observed over coated samples with the appearance of weak peaks at 2920 and 2850 cm^{-1} assigned to the stretching mode of CH_3 , and CH_2 groups. These observations cause to characteristics frequencies of residual organic species, which is not removed by drying under

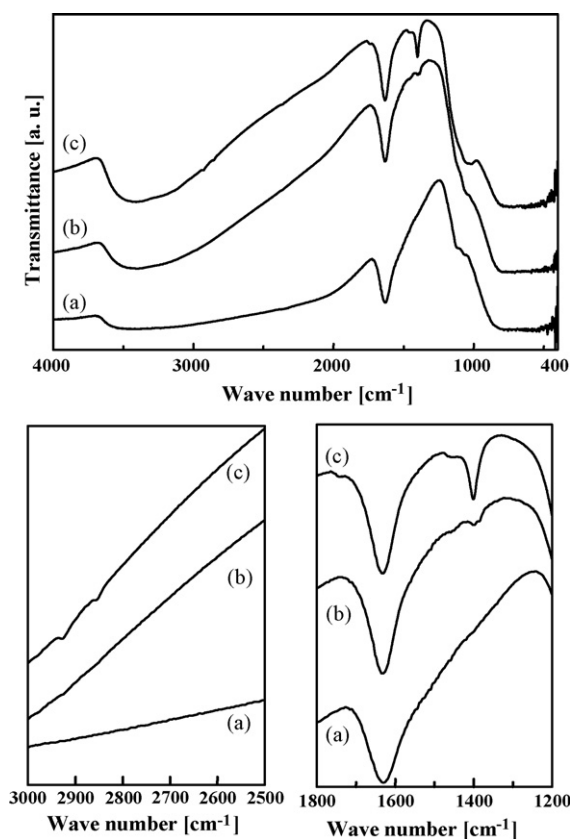


Fig. 1. FT-IR spectra of silica-coated TiO_2 particles prepared by microwave assisted sol–gel method (b) without catalyst, (c) with catalyst (pH 12), and (a) original TiO_2 particles.

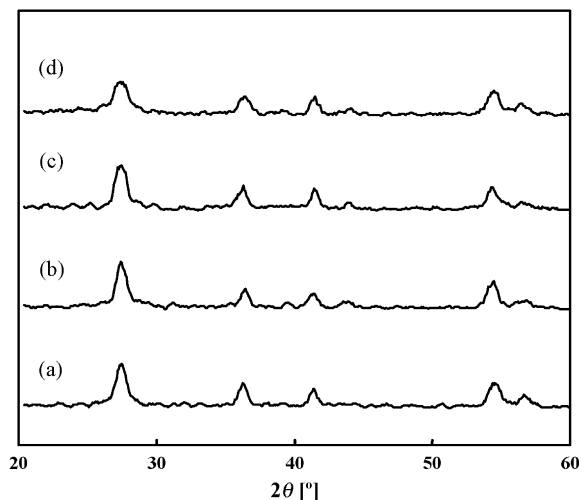


Fig. 2. XRD patterns of silica-coated TiO₂ particles prepared by microwave assisted sol–gel method (a) without catalyst, (b) with catalyst (pH 12), and by conventional sol–gel method (c) without catalyst, (d) with catalyst (pH 12).

vacuum at 353 K. Interestingly, the intensities of bands assigned to residual organic species increased with increasing in Si amounts on coated samples (Table 1). It indicates that residual organic species were derived from the ethoxy groups of TEOS, which did not convert to hydroxyl groups. These FT-IR results were also obtained over coated samples prepared by conventional sol–gel method.

Fig. 2 shows the XRD patterns of silica-coated TiO₂ particles prepared by microwave assisted sol–gel method and conventional sol–gel method. As can be seen from Fig. 2, four intense peaks appeared at $2\theta = 27.3^\circ$, 36.2° , 41.2° , 54.4° , which were assigned to the diffraction peaks of rutile TiO₂ [11–13,19,28]. The intensities of peaks assigned to rutile TiO₂ phase were maintained even after coating with silica. Additionally, the diffraction peaks due to silica were not observed over all coated samples which indicate that the structure of silica was amorphous phase. The average crystal size of rutile TiO₂ was determined from the broadening of the corresponding X-ray peaks at 27.3° by the Scherrer formula; $L = 0.90\lambda/\beta \cos \theta$, where L is crystal size of rutile TiO₂ (nm), λ is the wave length of X-ray source (Cu K α ; 0.15418 (nm)), β is the width of $I_{1/2\max}$. The calculated average crystal size in the range of 11–15 nm was in good agreement with primary particle size of original spindle shaped rutile TiO₂ (50 nm \times 15 nm). These results showed that all coated samples have amorphous phase of silica and rutile structure of TiO₂ with the average crystal size in the range of 11–15 nm.

Fig. 3 shows the particle size distribution of silica-coated TiO₂ fine particles prepared under (B) condition (Fig. 3(a)) and under (D) condition (Fig. 3(b)). Prior to this experiment, dried samples were dispersed in ethanol with grinding TiO₂ agglomerates in planetary ball mill. The maximum frequency of particle size distribution for silica-coated TiO₂ fine particles prepared under (B) and (D) conditions was 79 and 100 nm, respectively. Moreover, particle size distributions were sharp under both conditions which suggest that mono-dispersed silica-coated TiO₂ fine particles were obtained. Although the average size of primary particle was estimated 11–15 nm from XRD measurements (Fig. 2), agglomeration of TiO₂ fine particles in liquid phase cannot be avoided even after grinding in planetary ball mill. TiO₂ fine particles (50–100 nm) have potential for UV-ray shielding with their absorption, scattering, and reflecting [3] properties [4–6] as mentioned above. Therefore, these silica-coated TiO₂ particles can be used as UV filter in term of particle size. Mono-dispersed silica-coated TiO₂ particles (around 100 nm) were also obtained under other conditions without catalyst ((A) and (C)).

Fig. 4 shows the SEM images of silica-coated TiO₂ fine particles prepared under (C) condition (Fig. 4(a)) and (A) condition (Fig. 4(b)). The irregular shapes of particles were observed for silica-coated TiO₂ prepared by conventional sol–gel method, while spindle shaped particles were observed for one prepared by microwave assisted sol–gel method. The amounts of SiO₂ coated on TiO₂ surface were estimated to be the similar values (1.6–1.9 mol%, Table 2). For silica-coated TiO₂ prepared under (A) condition, there are two possibilities for observing similar shaped particles to original TiO₂ particles. One is that thin and uniformly layer of SiO₂ formed on TiO₂ surface. In some case, small sized

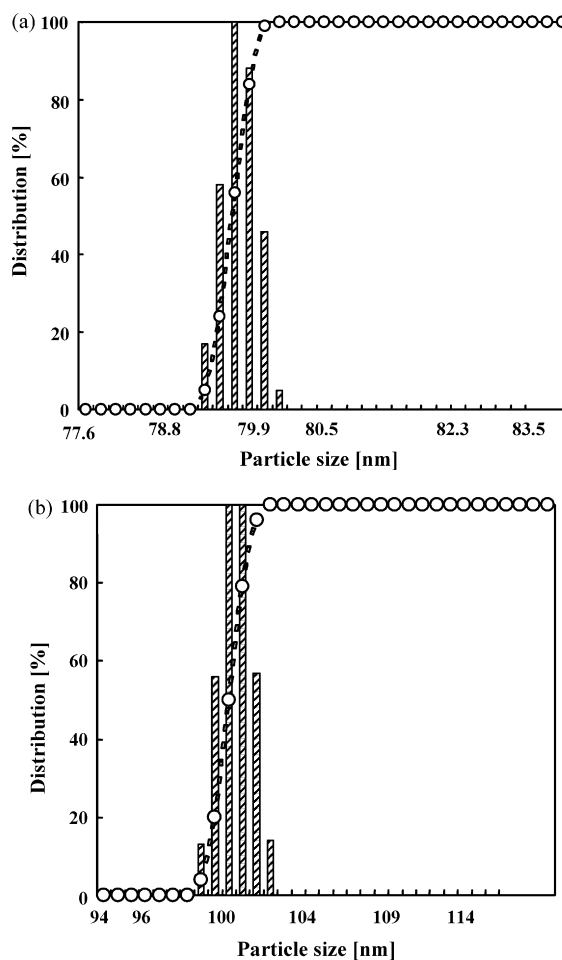


Fig. 3. Particle size distributions of silica-coated TiO_2 particles prepared by (a) microwave assisted sol-gel method with catalyst (pH 12) and (b) conventional sol-gel method with catalyst (pH 12).

SiO_2 particles were formed and these particles coated densely on TiO_2 particle surface. The other is that the nucleation of SiO_2 occurred and formed SiO_2 particles existed separately. A detailed discussion of this matter will be shown later.

MW processing of material is basically different from conventional processing in its heating mechanism. In a MW apparatus, heat is generated within sample itself by the interaction of MW with the material. Consequently, MW energy heats the material on a molecular level which leads to form uniform and nano-sized particles. On the other hand, in conventional sol-gel method (Fig. 4(a)), growth rates of SiO_2 coating layer on TiO_2 surface were localized because conventional method heats the material from exterior to interior which results in steep thermal gradients inside glass vessel. This different heating way causes different observations for samples.

Table 2

Photo-catalytic activities of physical mixtures of SiO_2 (SK14) and TiO_2 powders

Composition of physical mixture		Photo-catalytic activity (%)
SiO_2 (wt.%)	TiO_2 (wt.%)	
0	100	100
15	85	95
20	80	90
50	50	86

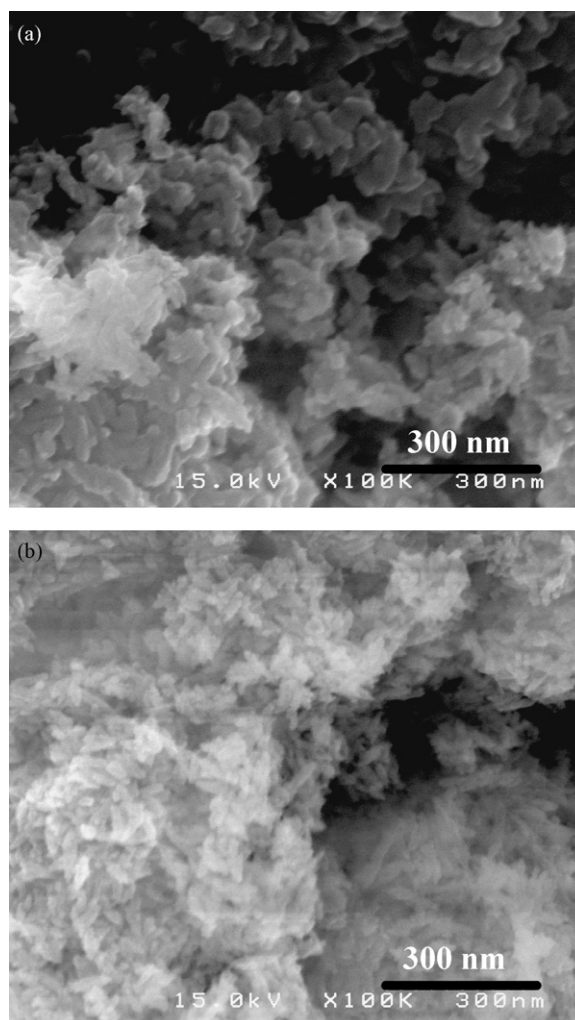


Fig. 4. SEM images of silica-coated TiO₂ particles prepared by (a) conventional sol-gel method without catalyst and (b) microwave assisted sol-gel method without catalyst.

The zeta potential–pH curves of samples were measured to check the surface coating effect on the dispersion of particles and the surface characteristics [9,13,17,18,29,30]. The variations of zeta potentials with pH values for non-coated TiO₂, silica-coated TiO₂, and SiO₂ (SK14, Mallinckrodt Inc., 100 mesh) particles are shown in Fig. 5. The isoelectric point (IEP) of non-coated TiO₂ is around pH 7.6, while the IEP of SiO₂ is around pH 3.2. In both samples, the zeta potential is positive below the IEP and negative above the IEP. It can be seen that silica-coated TiO₂ particles prepared under (B) and (D) conditions have the similar electrokinetic behavior as SiO₂. The zeta potential value of TiO₂ is about –18.3 mV at pH 8, whereas that of coated TiO₂ particles prepared under (B) and (D) condition is about –52 mV at pH 8, which enables the dispersion of coated TiO₂ particle to be much easier than non-coated TiO₂ particle. It shows that the surface characteristics of TiO₂ particle is changed after coating with silica and the surface structure of silica-coated TiO₂ particle is –Si–OH. The surface possess positive charge due to formation of –Si–OH₂⁺ when pH in the aqueous solution is lower than IEP, while the surface possess negative charge due to formation of –Si–O[–] when pH is higher than IEP [9,13].

On the other hand, the zeta potential–pH curve and IEP for coated TiO₂ particles prepared under (A) condition are similar to those of original TiO₂ particles. This result indicates that thin and uniformly layer of SiO₂ was not formed on TiO₂ particles. In combined with SEM observation result (Fig. 4(b)), it suggested that the nucleation of SiO₂ happened to form small sized SiO₂ particles, and then some of SiO₂ particles coated on TiO₂ surface or part of it existed

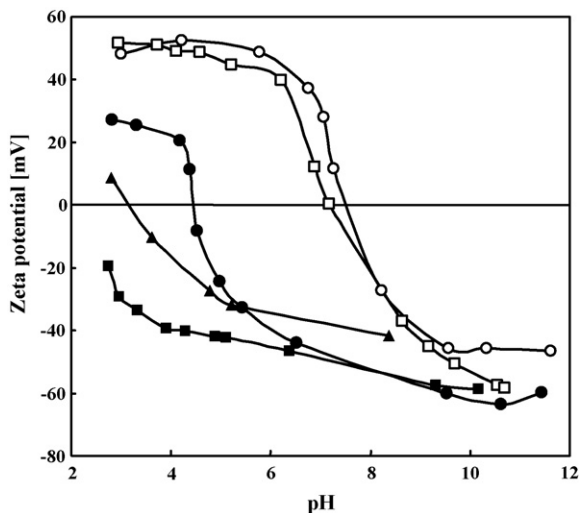


Fig. 5. The zeta potential curves of non-coated and coated TiO₂ particles as a function of pH values: (○) original TiO₂ particles; (□) coated TiO₂ particles prepared by microwave assisted sol-gel method without catalyst; (●) coated TiO₂ particles prepared by microwave assisted sol-gel method with catalyst; (▲) SiO₂ particles (SK14); (■) coated TiO₂ particles prepared by conventional sol-gel method with catalyst.

separately. Lin et al. [9] had reported that the zeta potential–pH curve and IEP for TiO₂ mixed with SiO₂ colloid were similar to those of pure TiO₂ particles. Part of SiO₂ colloid was adsorbed onto the surface of TiO₂ particles by electrostatic attraction and part of it remained in the solution. They concluded that the nucleation coating could not modify the TiO₂ particles effectively [9]. Therefore, the surface characteristics of coated TiO₂ prepared under (A) condition are essentially different from the coated TiO₂ prepared under (D) condition. The surface electrokinetic behavior depends on the quality of surface coating. Dense film coating can seal the TiO₂ particles completely and improve the particle dispersion, however, incomplete coating such as a nucleation coating shows less modification effect on TiO₂ particles.

TEM observations were conducted to check uniformity of SiO₂ coating on TiO₂ particles. Fig. 6 shows the TEM images of coated sample prepared under (A) condition (Fig. 6(a)), coated sample prepared under (D) condition (Fig. 6(b)), and non-coated TiO₂ (Fig. 6(c)). In Fig. 6(b), complete coating of SiO₂ leads that the shape of coated TiO₂ particles were completely different from that of original TiO₂ particles (Fig. 6(c)). The thickness of SiO₂ coating layer was estimated to be approximately 2 nm which is similar to the result of previous research [17]. This thickness value was smaller than the results reported in several researches [11–13]. Conversely, the coating of small sized SiO₂ particles on TiO₂ surface was observed on coated TiO₂ prepared under (A) condition (indicating in Fig. 6(a) by arrows). These observations indicated that dense film coating of SiO₂ layer was observed on sample prepared under (D) condition, however, the nucleation coating was observed on sample prepared under (A) condition. These results are good agreements with SEM observations (Fig. 4) and zeta potential results (Fig. 5).

3.2. Photo-catalytic activity and UV shielding ability

Fig. 7 shows the photo-catalytic activity and UV shielding ability of original TiO₂, silica-coated TiO₂ particles prepared under (A)–(D) conditions. The decreases in photo-catalytic activity and UV shielding ability were observed over highly SiO₂ (15–22 mol%, Table 1) coated TiO₂ surface (Fig. 7(d) and (e)). Although the photo-catalytic activity of both samples showed about 15% of original TiO₂ particles, UV shielding ability were different in both samples. The coated sample prepared under (B) condition showed 76% of original TiO₂ particles, however, 56% of original TiO₂ particles were obtained for coated sample prepared under (D) condition. These results indicated that the nucleation coating leads to maintain the UV shielding ability more effective than dense film coating. In Fig. 7(b) and (c), 50% of original TiO₂ for photo-catalytic activity and 100% of UV shielding ability reached on sample prepared under (A) condition, however, 58% of original TiO₂ for photo-catalytic activity and 92% of UV shielding ability were obtained for sample prepared under (C) condition. In any SiO₂ loading regions, the samples prepared by MW processing

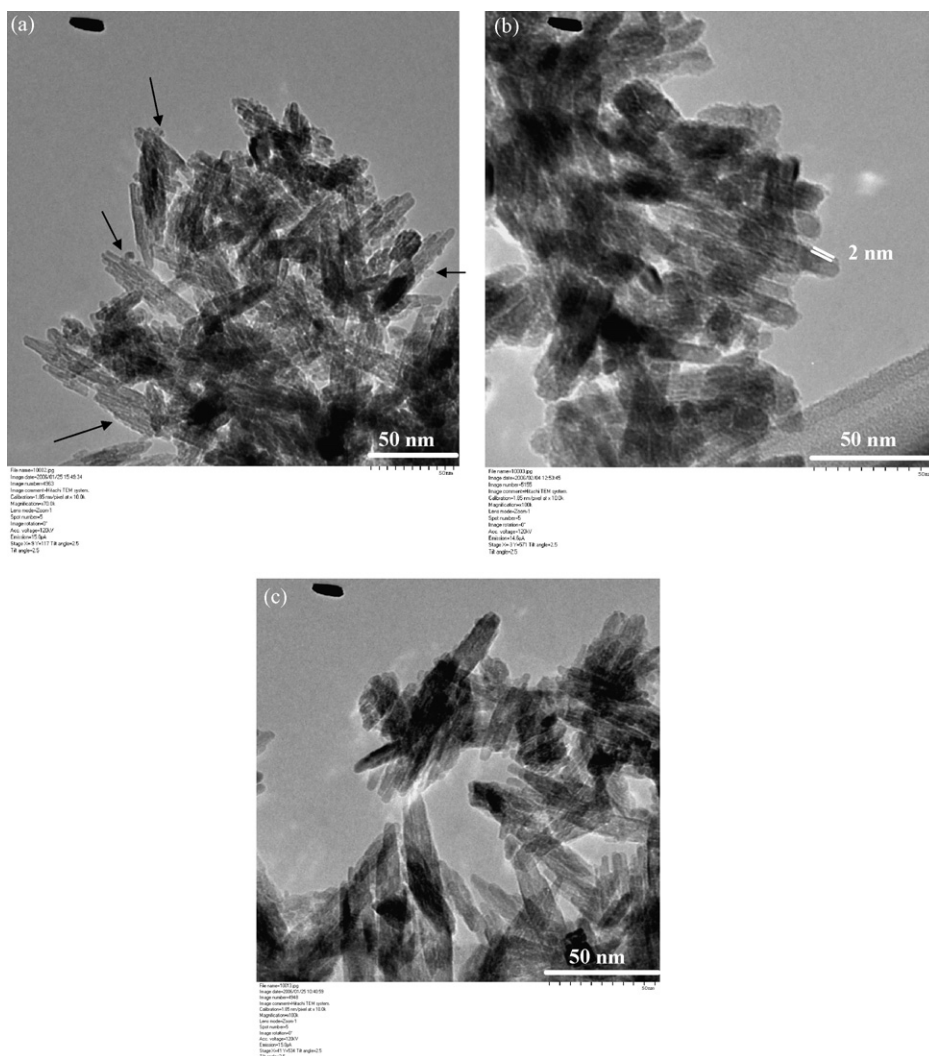


Fig. 6. TEM images of silica-coated TiO₂ particles prepared by (a) microwave assisted sol-gel method without catalyst, (b) conventional sol-gel method with catalyst, and (c) original TiO₂ particles.

showed higher inhibition of photo-catalytic activity and better UV shielding characteristics than the samples prepared by conventional method.

In Figs. 4–6, SEM, TEM, and zeta potential results showed that TiO₂ surface cannot be properly coated with SiO₂ particles by nucleation coating. We had checked the photo-catalytic activity of physical mixtures of SiO₂ and TiO₂ particles, and only 10% of inhibition extent for its photo-catalytic activity reached with 20 mol% of SiO₂ by physical mixture (Table 2). This result indicate that the chemical interaction between SiO₂ particles and TiO₂ fine particles must also occur to form coated sample in the case of microwave assisted sol-gel method because 50% of inhibition extent for photo-catalytic activity was attained over coated sample with only 1.6 mol% SiO₂ loading (Table 1, (A) condition). It was concluded from these results that the nucleation coating was not suitable for changing the surface characteristics, however, this coating way significantly affected the suppression of photo-catalytic activity and the maintenance of UV shielding ability. MW processing produced small and uniform SiO₂ particles, and TiO₂ surface was coated with these SiO₂ particles by a nucleation coating. Consequently, this coated sample suppress its photo-catalytic activity effectively, however, the reason is not clear until now. The studies on the consideration of this reason and the way of nucleation coating on TiO₂ surface densely will be next attempts.

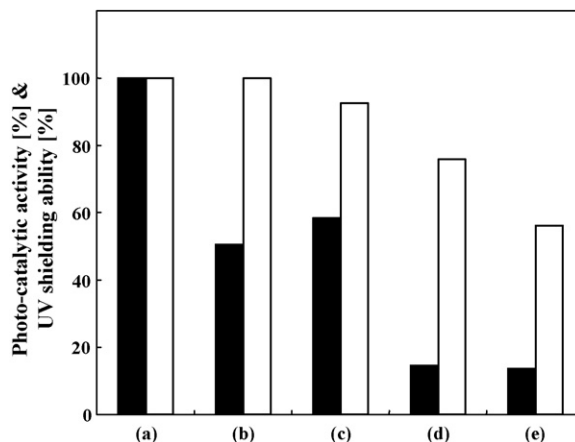


Fig. 7. Photo-catalytic activity and UV shielding ability of (a) original TiO₂ particles, (b) coated TiO₂ particles prepared by microwave assisted sol-gel method without catalyst, (c) conventional sol-gel method without catalyst, (d) microwave assisted sol-gel method with catalyst, and (e) conventional sol-gel method with catalyst; (■) photo-catalytic activity; (□) UV shielding ability.

4. Conclusion

The silica coating of TiO₂ surface was conducted to suppress its photo-catalytic activity with holding high ultraviolet (UV) shielding ability. Microwave (MW) assisted sol-gel method and conventional sol-gel method were performed in present study to discuss the effect of microwave on the property of silica-coated TiO₂ particles. In coated sample prepared by microwave assisted sol-gel method, all characterization results (BET surface area, X-ray photoelectron spectroscopy, X-ray fluorescence spectroscopy, scanning electron microscopy, transmission electron microscopy, zeta-potential) showed that MW processing produced small and uniform SiO₂ particles, and these particles coated on TiO₂ surface as a nucleation coating. On the other hand, dense film coating of SiO₂ layer with 2 nm of thickness were observed on coated TiO₂ particles prepared by conventional sol-gel method.

In any SiO₂ loading regions, the samples prepared by MW processing showed higher inhibition of photo-catalytic activity and better UV shielding ability than the samples prepared by conventional method. These results suggested that the kinds of silica coating significantly affected the photo-catalytic activity and UV shielding ability of coated TiO₂ particles.

Acknowledgement

The authors thank Takashi Kanda (Tokyo University of Science, Colloidal Assemblies and Surfaces Labo.) for the TEM measurements.

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