Available online at www.sciencedirect.com
ScienceDirect
Dyes and Pigments 76 (2008) 754–759
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

# Control of the photocatalytic activity of $TiO_2$ nanoparticles by silica coating with polydiethoxysiloxane

Iqbal Ahmed Siddiquey [a], Takeshi Furusawa [b], Masahide Sato [b], Kozue Honda [a], Noboru Suzuki [a,*]

[a] Department of Information and Control Systems Science, Graduate School of Engineering, Utsunomiya University, Yoto 7-1-2, Utsunomiya 321-8585, Japan
[b] Department of Applied Chemistry, Faculty of Engineering, Utsunomiya University, Japan

Received 5 September 2006; received in revised form 31 January 2007; accepted 31 January 2007
Available online 16 February 2007

**Abstract**

A novel, simple and fast coating method that is based on microwave (MW) irradiation and which uses polydiethoxysiloxane (PDES) has been developed for $TiO_2$ nanoparticles with the aim of reducing their photocatalytic activity. At the same time, silica coating was also carried out using a conventional solution method and the results of both methods were compared. The silica coated $TiO_2$ nanoparticles were characterized by X-ray photoelectron spectroscopy (XPS), zeta-potential analysis, Fourier transform infrared spectroscopy (FT-IR) and high-resolution transmission electron microscopy (HR-TEM). For both coating methods, the extent of silica coating was found to depend upon the PDES loading; Si content increased with increasing concentration of PDES. Silica coating effectively reduced the photocatalytic activity of the $TiO_2$ particles as evidenced by the color change of a mixture of non-coated and silica coated particles with 1,3-butanediol under UV radiation. The silica coated $TiO_2$ nanoparticles obtained using the MW irradiation method showed higher inhibition of photocatalytic activity and superior UV-shielding characteristics than particles coated using the conventional solution method.

*Keywords:* $TiO_2$; Photocatalytic activity; Silica coating; Microwave irradiation; Polydiethoxysiloxane; UV shielding

## 1. Introduction

Titanium dioxide nanoparticles enjoy manifold applications that include their usage as white pigment in the paint, plastic, and paper industries to their function as an inorganic UV-shielding material in the cosmetics industry. However, since $TiO_2$ (rutile) is also a semiconductor with a band gap of about 3.0 eV, solar UV radiation induces photocatalytic activity in the compound. Large particles of $TiO_2$ have been used as inorganic sunscreen materials for many years based on their ability to attenuate harmful UV radiation. However, a disadvantage in this context is that $TiO_2$-containing sunscreens have an opaque, white appearance due to the pigment's high scattering of visible light. While in conventionally sized, pigmentary $TiO_2$ particles, light scattering is governed by the Mie theory, in the case of ultrafine $TiO_2$ particles, Rayleigh's scattering theory applies. Thus, the finer the particle, the more effective is the scattering of UV light $<400$ nm. Moreover, if the particle size is reduced to the nanoscale, $TiO_2$ loses its characteristic white color and becomes transparent to visible light whilst still blocking UV rays. Unfortunately, transparency is not the only change characteristic of the nanosized metal oxide. While $TiO_2$ particles are generally considered to be inert in their larger form, nanosize particles are photocatalytically active, particularly in the presence of UV light. As a result, $TiO_2$ nanoparticles can exert strong oxidizing power and can produce highly reactive free radicals. Many applications of $TiO_2$ nanoparticles seek to harness this photocatalytic

---

* Corresponding author. Tel./fax: +81 28 689 6171.
*E-mail address:* suzukin@cc.utsunomiya-u.ac.jp (N. Suzuki).

0143-7208/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2007.01.020

property, including solar cell research, water cleanup techniques [1], and self-cleaning windows [2] that repel dirt in the presence of natural UV light. However, for sunscreen and other applications that require low photocatalytic activity, the ability to control this process would be of great value. To minimize their photocatalytic activity, $TiO_2$ particles need to be surface coated with an inert material, such as silica ($SiO_2$). A variety of chemical methods have been used for applying $SiO_2$ to the $TiO_2$ surface, such as phase transfer reactions between organic chloroform and aqueous phases [3], the Stöber process [4] and seeded polymerization [5]. However, most of these methods require long reaction times to hydrolyze the precursor completely. In recent work, we reported the use of a conventional solution method to silica coat $TiO_2$ nanoparticles which had been pre-coated with alumina [4]. However, while silica coating achieved in this way effectively suppressed the photocatalytic activity of $TiO_2$ nanoparticles, the large silica content tends to lower the UV-shielding ability of the coated material. This limitation represents a major hurdle in the application of these particles, particularly in sunscreen cosmetics. Alternatively, the MW irradiation method has been shown to offer a number of advantages over conventional solution methods, such as rapid and homogeneous heating throughout the reaction vessel, the possibility of selectively heating the desired materials and short reaction time. It has been shown that MW irradiation is an effective way to enhance the rate, yield and selectivity of chemical reactions; consequently, the number of applications of MW heating in chemistry is growing rapidly. For example, many reactions thought to require long reaction periods in biochemical applications and organic chemistry are ideal for rapid transformations using MW irradiation and do not require extensive heating. Recently, MW energy has been used in the field of materials science for synthesizing various composite ceramic powders at far lower temperatures and for shorter time periods than employed in conventional methods [6–11]. MW processing of materials differs fundamentally from conventional processing as heat is generated within the sample by the interaction of MW with the material [6–11]. MW energy heats the material at a molecular level which leads to uniform heating, whereas conventional energy heats the material from the exterior to the interior which results in steep thermal gradients. Thus, powders obtained by the MW route are superior in terms of compositional homogeneity [6,7].

The present work describes a simple, novel, and fast technique for the silica coating of $TiO_2$ nanoparticles using MW irradiation and a polymeric precursor, polydiethoxysiloxane (PDES). An advantage of this coating method is the short reaction time, as the formation of silica coated particles takes only 2 min. The results obtained with MW irradiation are compared with those produced using a conventional solution method. It is important to note that the objective of the MW irradiation method is not to coat the $TiO_2$ surface with more silica but rather to inhibit photocatalytic activity using the thinnest coating of silica possible so as to maximize the UV-shielding properties of the coated particles.

## 2. Experimental

### 2.1. Materials

The list of samples prepared in this study and the key differences in their preparation are shown in Table 1. Silica coating was carried out on commercial rutile $TiO_2$ (MT-150W) purchased from Tayca Corporation, Japan. Polydiethoxysiloxane (PDES) with a unit $M_r$ of 134.2 (Gelest, Inc.) and 1,3-butanediol (Kanto Chemical Co. Inc., purity 98%) were used as received. All other chemicals were of reagent grade and were used without further purification.

### 2.2. Silica coating methods

#### 2.2.1. Conventional solution method

$TiO_2$ dispersions were prepared by ball-milling (Pulverisette-7, Fritsch GmbH, Germany). Non-coated $TiO_2$ nanoparticles (2.5 g) were placed along with 20 ml of ethanol with 73.2 g zirconia balls (0.5 mm in diameter) as grinding media in a milling pot. Grinding was carried out for 10 min by rotating the vessel at 370 rpm. The $TiO_2$ dispersion was then slowly transferred to a 500-ml round-bottom flask and an appropriate amount of PDES together with 85 ml of ethanol, 45 ml water and 30 ml aq. $NH_4OH$ ($pH = 12$) was added. Coating was allowed to proceed for 6 h at room temperature with vigorous stirring. The coated $TiO_2$ particles were collected by centrifugation, washed with ethanol three times and then dried in a vacuum oven at 110 °C for 2 h.

#### 2.2.2. MW irradiation method

The $TiO_2$ dispersion was prepared by the aforementioned procedure. A mixture containing the $TiO_2$ dispersion, PDES, solvent, and aq. $NH_4OH$ ($pH = 12$) solution was irradiated in a Shikoku Keisoku SMW 064, 2.4 GHz, maximum power 500 W, MW apparatus containing a built-in magnetic stirrer plate coated with PTFE. The temperature of the mixture was 70 °C, controlled by a thermocouple inserted through a hole in the top of the MW apparatus. MW irradiation was carried out for 2 min and the silica coated particles were collected and washed, using the procedure described in the conventional solution method.

### 2.3. Photocatalytic activity measurement

To measure the photocatalytic activity of the samples, either non-coated or silica coated $TiO_2$ and 1,3-butanediol

Table 1
Sample names and coating conditions

| Conventional solution method | | Microwave irradiation method | |
|---|---|---|---|
| Sample name | PDES/$TiO_2$ starting ratio (wt/wt) | Sample name | PDES/$TiO_2$ starting ratio (wt/wt) |
| PDES-10 wt% | 0.1 | MW-PDES-10 wt% | 0.1 |
| PDES-30 wt% | 0.3 | MW-PDES-30 wt% | 0.3 |
| PDES-50 wt% | 0.5 | MW-PDES-50 wt% | 0.5 |
| PDES-80 wt% | 0.8 | MW-PDES-80 wt% | 0.8 |

were mixed in the ratio of 4:3 (by mass) for 3 min, after which the resulting paste was placed between a pair of microscope slide glasses. Exposure of the paste to UV radiation photoreduced the $TiO_2$ such that the color of the paste changed from white to blue [12]. The CIE $L^*a^*b^*$ color difference ($\Delta E^*$) before and after 1 h exposure to UV radiation was measured using an NF 333, Nippon Denshoku Industries Co., Ltd., Japan digital spectrophotometer. The average UV-A and UV-B exposure intensities for all measurements were around 80 and 0.25 $Wm^{-2}$, as determined using a MS-211-I, Eko Instruments Co., Ltd., Japan UV monitor. Three plates were prepared for each sample and the averages of seven successive measurements were used. The relative photocatalytic activity of the coated samples was calculated according to Eq. (1)

$$\text{Photocatalytic activity } (\%) = 100 \times \Delta E^*(\text{silica coated TiO}_2)/\Delta E^*(\text{non-coated TiO}_2) \qquad (1)$$

### 2.4. Surface characterization

XPS analyses were carried out using a Physical Electronics ESCA-5600 spectrometer equipped with a Mg Kα X-ray source operating at 200 W (15 kV, 13 mA). The vacuum in the main chamber was kept $>3 \times 10^{-7}$ Pa during XPS data acquisition. Specimens were analyzed at an electron take-off angle of 45°, with respect to the surface plane. For all samples, general survey scans (binding energy range: 0–800 eV, pass energy: 187.5 eV) and high-resolution spectra (pass energy: 23.50 eV) in the regions of C 1s, Si 2p, O 1s, and Ti 2p were recorded. Binding energies were referenced to the C 1s binding energy at 284.8 eV. The zeta-potential of the $TiO_2$ and silica coated $TiO_2$ particles was measured using a Zeta Plus apparatus (Brookhaven Instr. Corp., USA); particles (0.02 g) were mixed with 200 ml distilled water and the mixtures were sonicated for 30 min; the pH was adjusted by the addition of 0.1 M HCl or NaOH aqueous solution.

FT-IR spectra were recorded in transmission mode with KBr pellets using an FT/IR-400 spectrometer (Jasco Corp., Japan), collecting 16 scans in the 4000–400 $cm^{-1}$ range with 4 $cm^{-1}$ resolution. To determine the uniformity and thickness of the silica coating, a Hitachi H-7650 high-resolution transmission electron microscope was used to obtain HR-TEM micrographs.

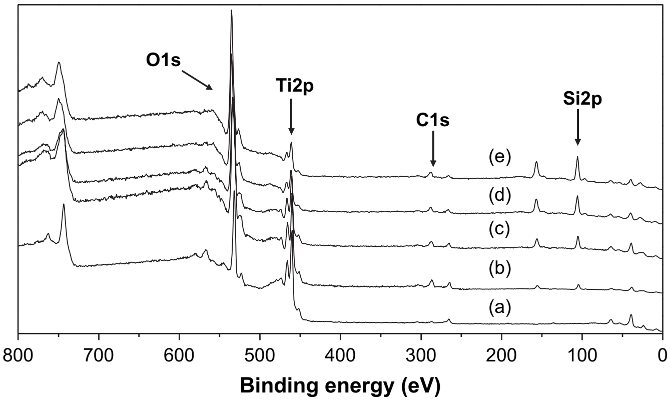

Fig. 1. XPS spectra of (a) non-coated and silica coated $TiO_2$ nanoparticles; (b) PDES-10 wt%; (c) PDES-30 wt%; (d) PDES-50 wt%; and (e) PDES-80 wt%.

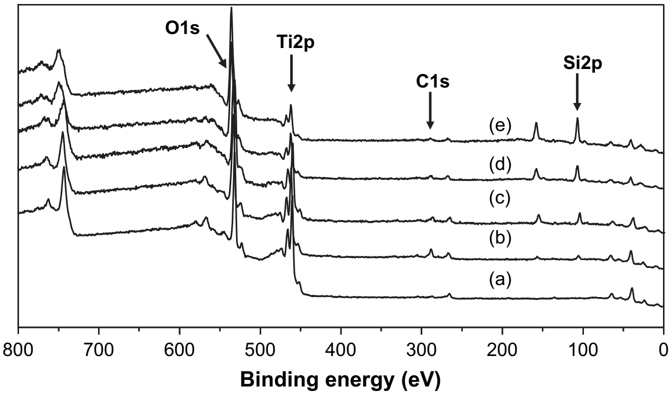

Fig. 2. XPS spectra of (a) non-coated and silica coated $TiO_2$ nanoparticles; (b) MW-PDES-10 wt%; (c) MW-PDES-30 wt%; (d) MW-PDES-50 wt%; and (e) MW-PDES-80 wt%.

The UV-shielding properties of the particles were evaluated by measuring the transmittance of a film to which uniformly dispersed sample powder had been applied. The dispersion mixture was prepared by uniformly mixing 0.1 g of sample powder, 0.15 g of liquid paraffin oil and 10 ml of nitrocellulose for 10 min at 370 rpm using a planetary ball mill charged with 40 g of zirconia balls. The resulting dispersion was applied to polypropylene film and the UV–vis transmittance of the ensuing film was measured with a UV–vis spectrophotometer (Jasco Corp., V-560).

## 3. Results and discussion

The chemical states of the atoms on the $TiO_2$ surface and in the layer of silica coating were examined by XPS analysis. Figs. 1 and 2 show the wide scan XPS spectra of both the non-coated and $TiO_2$ nanoparticles coated with PDES. The spectra of both the non-coated and silica coated particles showed the presence of Ti, O, and C. The C 1s peaks can be assigned to carbon contamination. In contrast to the spectra of the non-coated $TiO_2$ particles that of the silica coated particles contained Si 2p peaks, which indicated that the $TiO_2$ particle surface had indeed been coated with silica. The relative surface compositions of the coated particles, as derived from the XPS peak intensities, are shown in Table 2, which

Table 2
Elemental composition of samples from XPS analysis

| Sample | Elemental composition (at.%) | | | |
|---|---|---|---|---|
| | Ti | O | Si | C |
| PDES-10 wt% | 20.3 | 66.4 | 4.0 | 9.1 |
| PDES-30 wt% | 13.3 | 68.6 | 10.9 | 6.1 |
| PDES-50 wt% | 8.8 | 69.4 | 17.2 | 4.4 |
| PDES-80 wt% | 6.3 | 68.7 | 20.9 | 4.1 |
| MW-PDES-10 wt% | 20.3 | 66.4 | 4.0 | 9.1 |
| MW-PDES-30 wt% | 13.5 | 70.7 | 11.8 | 4.8 |
| MW-PDES-50 wt% | 9.8 | 71.5 | 15.3 | 3.3 |
| MW-PDES-80 wt% | 7.5 | 71.1 | 19.1 | 2.2 |

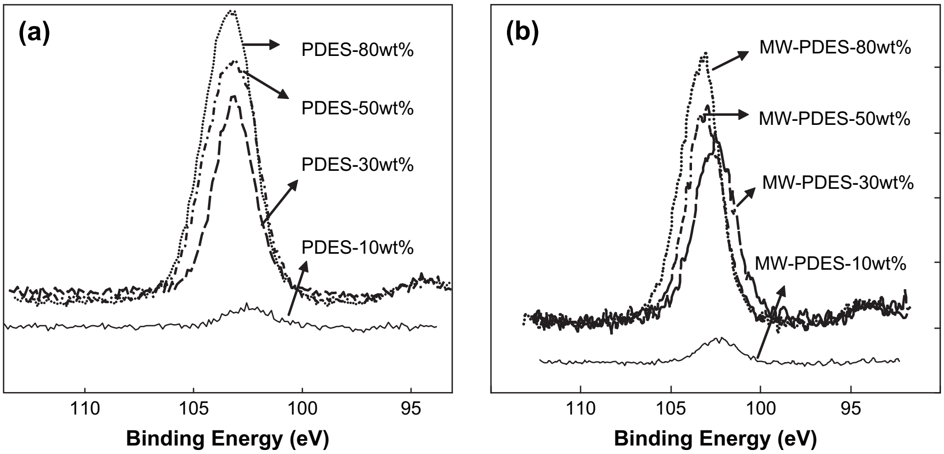

Fig. 3. The XPS narrow scan spectra of Si 2p for silica coated $TiO_2$ nanoparticles obtained by (a) the conventional solution method and (b) the MW irradiation method.

demonstrate that the MW irradiation method was as effective as the conventional solution method in terms of coating the $TiO_2$ particles with silica. The data in the table clearly reveal that, in both methods, the Si content of the coated particles is a function of the PDES loading and increases with increasing the ratio of PDES/$TiO_2$ nanoparticles. In addition, the Ti content clearly decreased while the O content remained largely unchanged.

The XPS narrow scan spectra of Si 2p for the silica coated $TiO_2$ particles are shown in Fig. 3. All of the binding energies of Si 2p for the silica coated $TiO_2$ particles obtained by the conventional method were lower than those of bare silica [13]. The peak of Si 2p at a PDES/$TiO_2$ ratio of 0.1 was located at around 102.5 eV. However, it can be seen that the binding energy of Si 2p gradually increased from 102.5 to 103.2 eV when the PDES/$TiO_2$ ratio increased from 0.1 to 0.8 i.e. as the Si content increased, the Si 2p binding energy approached that of bulk $SiO_2$ (103.35 eV) [13]. A similar trend was observed for the silica coated samples obtained using the MW irradiation method. In the latter case, the binding energy of Si 2p increased from 102.2 to 103.0 eV when the PDES/$TiO_2$ ratio increased from 0.1 to 0.8.

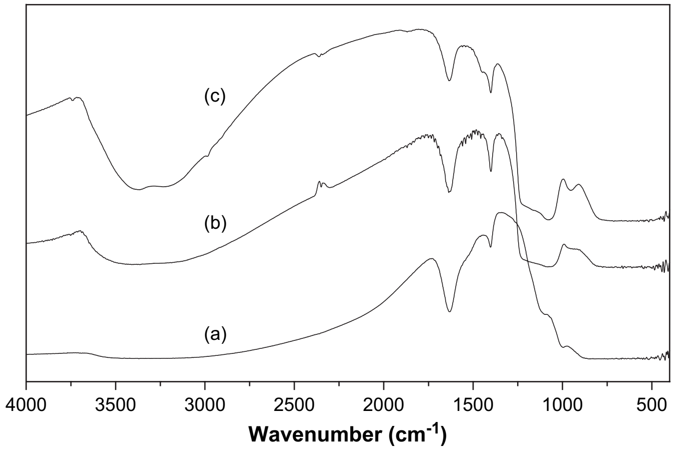

Fig. 4. FT-IR spectra of (a) non-coated and silica coated $TiO_2$ nanoparticles obtained by (b) MW irradiation and (c) conventional solution method.

Fig. 4 shows the FT-IR spectra of both non-coated and silica coated $TiO_2$ nanoparticles. The broad band at around 3300 $cm^{-1}$ and the sharp band at around 1625 $cm^{-1}$ present in both native and silica coated $TiO_2$ particles are due to adsorbed water on the $TiO_2$ [14,15]. It can be seen that, compared with the spectrum of non-coated $TiO_2$, a dominant broad band at 1040–1187 $cm^{-1}$ was present in the spectra of the silica coated $TiO_2$ particles obtained using both methods. This peak can be assigned to (Si–O–Si) asymmetric stretching vibration and confirms the silica coating of $TiO_2$ [16].

The variations in zeta-potential with respect to pH for both non-coated and silica coated $TiO_2$ are presented in Fig. 5. The surface charge on $TiO_2$ in pure water results from the pH-dependent speciation of the surface hydroxyl groups, which is described by the following reactions:

$$\equiv \mathrm{Ti} - \mathrm{OH}_2^+ \leftrightarrow \equiv \mathrm{Ti} - \mathrm{OH} + \mathrm{H}^+ \qquad (2)$$

$$\equiv \mathrm{Ti} - \mathrm{OH} \leftrightarrow \equiv \mathrm{Ti} - \mathrm{O}^- + \mathrm{H}^+ \qquad (3)$$

As the isoelectric point (IEP) of $TiO_2$ is around pH 3.6, the $TiO_2$ surface is negatively charged at pH > 3.6 and positively charged at pH < 3.6. Apparently, the zeta-potential differed after

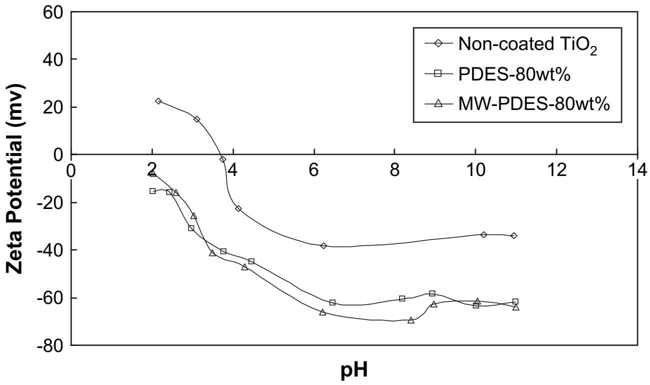

Fig. 5. Variation of zeta-potential with pH for non-coated and silica coated $TiO_2$ nanoparticles.

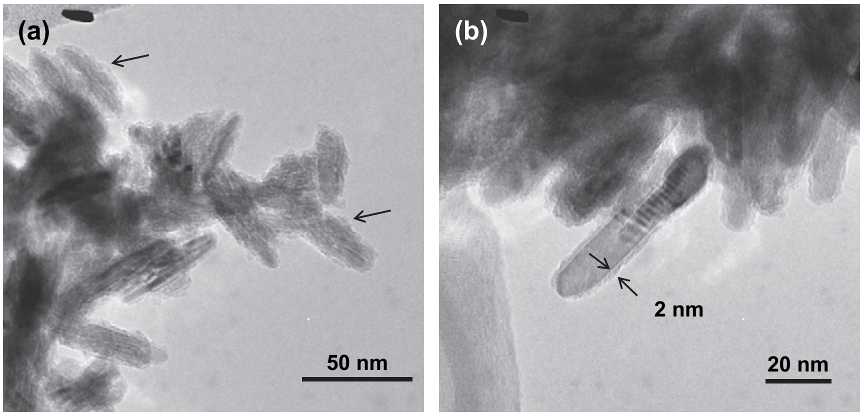

Fig. 6. HR-TEM micrographs of silica coated $TiO_2$ nanoparticles by (a) the conventional solution method and (b) the MW irradiation method.

silica coating, indicating that the surface properties of the coated $TiO_2$ particles had changed. It should be noted that the isoelectric point of silica coated $TiO_2$ shifted significantly at lower pH and that the surface charge of the coated $TiO_2$ was more negative than that of pure $TiO_2$ over the whole pH range studied. The zeta-potential of non-coated $TiO_2$ particles at pH 7 was around −38 mV whereas that of silica coated $TiO_2$ particles was −61 and −71 mV for particles obtained by the conventional and MW irradiation method, respectively. This confirmed the superior dispersion of coated particles than of non-coated particles.

Fig. 6 shows the HR-TEM micrographs of $TiO_2$ nanoparticles coated with silica using both the conventional and MW irradiation methods; the weight ratio of PDES/$TiO_2$ nanoparticles was 0.8 in both cases. The HR-TEM micrographs reveal that a uniform and continuous coating layer was formed around the surface of the spindle-shaped $TiO_2$ nanoparticles using the MW irradiation method. The thickness of the silica layer was estimated to be about 2 nm. In addition, the uniformity of the coating layer was significantly affected by the silica coating method. The uniform heating produced by MW resulted in uniform coating of the particles, in contrast to the conventional coating method (Fig. 6a), which produced a non-uniform and discontinuous coating.

The photocatalytic activities of the non-coated and silica coated samples were evaluated by measuring the color change of mixtures of non-coated or silica coated $TiO_2$ with 1,3-butanediol after UV irradiation. Fig. 7 shows the photocatalytic activity of the $SiO_2$ coated $TiO_2$ particles compared to those of the non-coated sample (100%). These results indicate that the photocatalytic activity of silica coated $TiO_2$ particles was effectively suppressed. The observed trend in the inhibition of photocatalytic activity was consistent with the increase in Si content, as calculated from quantitative XPS analysis. It was evident that, for a PDES/$TiO_2$ ratio of 0.8:1, the photocatalytic activity of the sample prepared using the MW irradiation method decreased to 10.3% compared with 13% for the sample prepared by the conventional solution method, which may have been due to the uniform heating and thus the uniform coating, produced by the MW method. The results further indicate that the properties conferred by silica coating of the $TiO_2$ surface are a function not only of the amount of silica used to coat the particle, but also of the coating method used.

The UV–vis transmittance spectra of non-coated and silica coated $TiO_2$ are presented in Fig. 8. The transmittance spectra showed that silica coating of $TiO_2$ using PDES does not markedly reduce the transmittance of $TiO_2$. Both non-coated and silica coated particles displayed good transparency in the visible region. UV shielding decreased as a result of silica coating due to a reduction in Ti content. However, the UV-shielding characteristics of the silica coated particles prepared by MW irradiation were better than those of particles obtained by the conventional solution method.

## 4. Conclusions

A simple, fast, and novel method based on MW irradiation using polydiethoxysiloxane has been successfully developed for the silica coating of $TiO_2$ nanoparticles. HR-TEM micrographs showed that the MW method yielded $TiO_2$ nanoparticles that were uniformly coated with $SiO_2$. Thus, by taking advantage of the rapid and uniform heating provided by MW irradiation, silica coated $TiO_2$ nanoparticles obtained by microwave irradiation displayed superior inhibition of photocatalytic

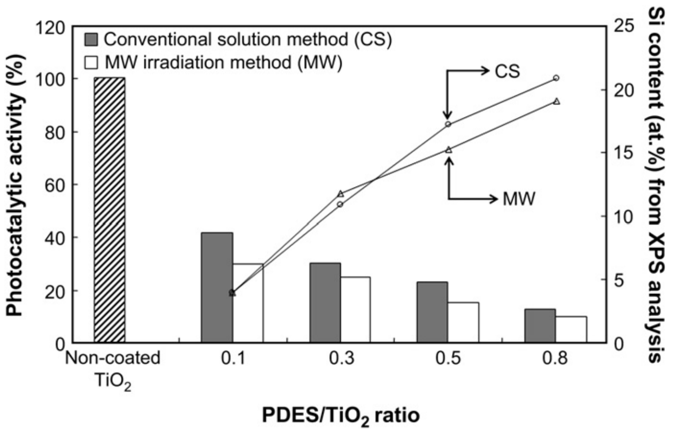

Fig. 7. Photocatalytic activity of non-coated and silica coated $TiO_2$ nanoparticles.

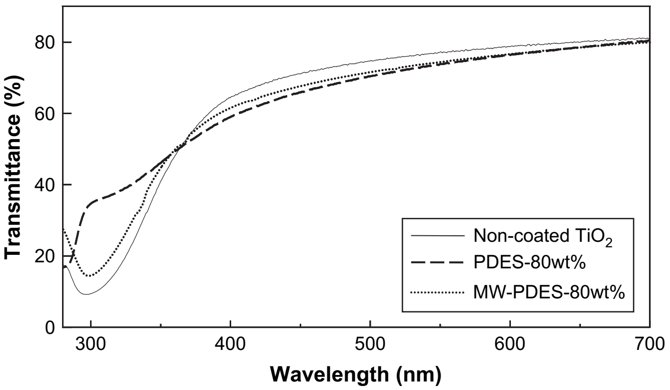

Fig. 8. UV−vis transmittance spectra of non-coated and silica coated $TiO_2$ nanoparticles.

activity and better UV-shielding properties than those prepared by a conventional solution method.

## Acknowledgements

This work was financially supported by Venture Business Laboratory of Utsunomiya University as young scholarship project. The technical assistance from Prof. M. Abe and his lab staff of the Tokyo University of Science is greatly appreciated.

## References

[1] Ilisz I, Dombi A, Mogyorosi K, Dekany I. Photocatalytic water treatment with different $TiO_2$ nanoparticles and hydrophilic/hydrophobic layer silicate adsorbents. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2003;230(1−3):89−97.

[2] Blount MC, Kim DH, Falconer JL. Transparent thin-film $TiO_2$ photocatalysts with high activity. Environmental Science and Technology 2001;35(14):2988−94.

[3] Ok KP, Young SK, Beong GJ. Synthesis of $TiO_2$ nanoparticles coated with $SiO_2$ for suppression of photocatalytic activity and dispersion stability. Journal of Industrial and Engineering Chemistry 2004;10(5):733−8.

[4] Ukaji E, Harigaye K, Furusawa T, Sato M, Suzuki N. The silica coating of fine $TiO_2$ particles by sol−gel process and its effects on the photocatalytic activity and UV-shielding ability. Material Technology 2006;24(5):275−81.

[5] Ahmed ME, Shu Y, Tsugio S. Control of silica shell thickness and microporosity of titania−silica core-shell type nanoparticles to depress the photocatalytic activity of titania. Journal of Colloid and Interface Science 2006;300:123−30.

[6] Kiminami RHGA, Morelli MR, Folz DC, Clark DE. Microwave synthesis of alumina powders. American Ceramic Society Bulletin 2000;79(3): 63−7.

[7] Ganesh I, Srinivas B, Johnson R, Saha BP, Mahajan YR. Microwave assisted solid state reaction synthesis of $MgAl_2O_4$ spinel powders. Journal of the European Ceramic Society 2004;24(2):201−7.

[8] Ganesh I, Johnson R, Saha BP, Rao GVN, Mahajan YR, Madavendra SS, et al. Microwave-assisted combustion synthesis of nanocrystalline $MgAl_2O_4$ spinel powder. Ceramics International 2004;31(1):67−74.

[9] Michael D, Mingos P, Baghurst DR. Applications of microwave dielectric heating effects to synthetic problems in chemistry. Chemical Society Reviews 1991;20(1):1−47.

[10] Rao KJ, Ramesh PD. Use of microwaves for the synthesis and processing of materials. Bulletin of Materials Science 1995;18(4):447−65.

[11] Fu Y-P, Lin C-H. Preparation of $Ce_xZr_{1-x}O_2$ powders by microwave-induced combustion process. Journal of Alloys and Compounds 2003;354(1−2):232−5.

[12] Jacobsen AE. Titanium dioxide pigments; correlation between photochemical reactivity and chalking. Industrial and Engineering Chemistry 1947;41(3):523−6.

[13] Tada H. Photoinduced oxidation of methylsiloxane monolayers chemisorbed on $TiO_2$. Langmuir 1996;12(4):966−71.

[14] Deng C, James PF, Wright PV. Poly(tetraethylene glycol malonate)−titanium oxide hybrid materials by sol−gel methods. Journal of Materials Chemistry 1998;8(1):153−9.

[15] Park HK, Kim DK, Kim CH. Effect of solvent on titania particle formation and morphology in thermal hydrolysis of $TiCl_4$. Journal of the American Ceramic Society 1997;80(3):743−9.

[16] Liden E, Bergstroem L, Persson M, Carlsson R. Surface modification and dispersion of silicon nitride and silicon carbide powders. Journal of the European Ceramic Society 1991;7(6):361−8.