

# Hot-water treatment of sol–gel derived SiO<sub>2</sub>–TiO<sub>2</sub> microparticles and application to electrophoretic deposition for thick films

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**Abstract** SiO<sub>2</sub>–TiO<sub>2</sub> spherical microparticles of about 0.7 μm in diameter were prepared by the sol–gel method. Anatase nanocrystals were formed in the microparticles and their specific surface area was increased after a hot-water treatment at 90 °C. From the changes in the concentration of I<sub>2</sub> photocatalytically generated from KI aqueous solution, the activity of the SiO<sub>2</sub>–TiO<sub>2</sub> microparticles was found to increase with increasing the hot-water treatment time. Particulate, thick films were electrophoretically deposited on indium tin oxide (ITO)-coated glass substrates using the anatase nanocrystal-precipitated SiO<sub>2</sub>–TiO<sub>2</sub> microparticles. The thickness of the electrophoretically deposited particulate film increased to be approximately 10 μm with an increase in applied voltage. The resultant thick film showed a high photocatalytic activity.

## Introduction

TiO<sub>2</sub>-based microparticles and films are the subject of an extensive research aiming at the applications as

photocatalysts for environmental purification, photo-induced superhydrophilic coatings, and electrodes of dye-sensitized photochemical solar cells [1–9]. The control of the nanostructures of the TiO<sub>2</sub>-based microparticles and thickness of the particulate films further offers an exciting opportunity to enhance their unique physical and chemical properties. The performance of their photocatalytic reactions depends on the characteristics of the TiO<sub>2</sub> crystallites, such as the size and surface area. TiO<sub>2</sub> nanocrystals show higher photocatalytic activities than the bulk, since the nano-sized crystals have a large surface area per unit mass which facilitates the diffusion of excited electrons and holes towards the surface before their recombination. A high dispersion of the nanocrystals in the host matrix without aggregation is also important to enhance the activity. A large surface area, high transmittance of UV light, and durability against photocatalytic activity are required for the host matrix in which the nanocrystals are dispersed. Silica gel is a candidate matrix for meeting these requirements. Therefore, various kinds of SiO<sub>2</sub>–TiO<sub>2</sub> nanocomposite microparticles and films have been studied for photocatalytic, superhydrophilic, and solar cell applications [10–13].

We have shown that anatase nanocrystals are formed on sol–gel derived SiO<sub>2</sub>–TiO<sub>2</sub> coatings upon hot-water treatment at 97 °C for 1 h [14, 15]. In the hot-water treatment, substrates with coatings are immersed into hot, pure water and kept at rest for a given time. The formation of anatase nanocrystals is rarely observed in the pure TiO<sub>2</sub> coating under the same conditions. High photocatalytic activities of the anatase nanocrystal-dispersed coatings have been demonstrated by the decomposition and oxidation of acetaldehyde, NO<sub>x</sub>, methylene blue, and potassium

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iodide [16–18]. Although it takes a longer period of time, considerable amounts of anatase nanocrystals are formed on the  $\text{SiO}_2\text{--TiO}_2$  coatings even at 38 °C after a treatment of 65 h [19]. The amounts of anatase nanocrystals formed by hot-water treatment are maximized for the  $\text{SiO}_2\text{--TiO}_2$  coatings with  $\text{TiO}_2$  contents of around 25 mol% [20].

On the other hand, electrophoretic deposition is a promising technique for the fabrication of novel nanostructured and nanoscaled materials, including the use of nanoparticles, nanosheets, nanotube, and related nanomaterials [21]. Electrophoretic deposition of thin and thick films of crystalline  $\text{TiO}_2$  has been extensively investigated. Commercially available  $\text{TiO}_2$  nanoparticles are widely used for the production of particulate titania films on electronically conducting glass substrates, metallic plates, and SiC fibers, the applications of which are photovoltaic cells, photocatalysts, protective coatings, biocompatible materials, etc. [22–24]. A significant improvement of the electrophoretic deposition has been achieved by the so-called electrophoretic sol–gel deposition combining particle preparation by the sol–gel method and film formation by the electrophoretic deposition method. Thick films of  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and organically modified  $\text{SiO}_2$  about several micrometer in thickness have been prepared by the method using sol–gel derived particles from the corresponding alkoxides [25–28], whereas there are few reports of the preparation of thick films consisting of titania nanocrystal-dispersed  $\text{SiO}_2\text{--TiO}_2$  particles by the electrophoretic sol–gel deposition.

In this study,  $\text{SiO}_2\text{--TiO}_2$  spherical microparticles were prepared by the sol–gel method. The  $\text{SiO}_2\text{--TiO}_2$  microparticles were treated with hot water to form anatase nanocrystals in the microparticles. The changes in structure, texture, crystallinity, specific surface area, and photocatalytic activity of the resultant microparticles were evaluated. Thick films of particulate  $\text{SiO}_2\text{--TiO}_2$  with a high photocatalytic activity were formed on the electronically conducting substrates by the electrophoretic deposition using the hot-water treated microparticles.

## Experimental procedure

### Preparation and characterization of hot-water treated $\text{SiO}_2\text{--TiO}_2$ particles

Silicon tetraethoxide ( $\text{Si}(\text{OEt})_4$ ) and titanium tetra-*n*-butoxide ( $\text{Ti}(\text{O-}n\text{-Bu})_4$ ) were used as the starting materials. Ethanol (EtOH) and hydroxylpropylcellulose (HPC) were selected as the solvent and the

dispersant, respectively.  $\text{Si}(\text{OEt})_4$  dissolved in EtOH was hydrolyzed with distilled water at room temperature for 0.5 h. The hydrolyzed  $\text{Si}(\text{OEt})_4$  solution was added to the EtOH solution containing  $\text{Ti}(\text{O-}n\text{-Bu})_4$  and HPC, and stirred for various times from 0.5 to 21.5 h. The molar ratio of  $\text{Si}(\text{OEt})_4\text{:Ti}(\text{O-}n\text{-Bu})_4\text{:H}_2\text{O:EtOH}$  in the suspension thus obtained was 5:1:23:300. The concentration of HPC in the suspension was 0.1 mass%. The  $\text{SiO}_2\text{--TiO}_2$  microparticles were collected by centrifugation using a KUBOTA centrifugal separator with cooling system 1710 from the colloidal suspension and dried under vacuum using an ETAC THERMOVAC VT220. The dried  $\text{SiO}_2\text{--TiO}_2$  microparticles were dispersed in hot water at 90 °C and stirred for various times from 0 to 4 h.

Scanning electron microscopes (SEM) (JEOL, JSM-5300 and Hitachi, S-4500) were used for the observation of shape and size of the particles and for the estimation of the film thickness. The structure and chemical composition of the  $\text{SiO}_2\text{--TiO}_2$  microparticles were evaluated using a Fourier transform infrared (FT-IR) spectrophotometer (Perkin-Elmer, Spectrum GX) and an energy-dispersive X-ray (EDX) spectrophotometer (JEOL, Model JED-2001) equipped with JSM-5300, respectively. FT-IR spectra of the particles were obtained by KBr method. Crystallinity of the microparticles was examined by X-ray diffractometer (Rigaku, RINT1100) and transmission electron spectroscopy (TEM) (Hitachi, HF-2000). Zeta potentials of the  $\text{SiO}_2\text{--TiO}_2$  microparticles were evaluated using a Malvern Instrument Zetamaster. Specific surface area of the particles was measured by BET methods using a Micromeritics Tristar 3000.

Photocatalytic activity of  $\text{SiO}_2\text{--TiO}_2$  microparticles was evaluated from the amounts of photogenerated  $\text{I}_2$  in potassium iodide (KI) aqueous solutions during UV irradiation.  $\text{SiO}_2\text{--TiO}_2$  microparticles (1 mg) were dispersed in  $0.1 \text{ mol dm}^{-3}$  KI aqueous solution (2 mL) in a Pyrex<sup>®</sup> spectrophotometer cell and the cell was irradiated with UV light using a black light (FL20S BL-B 20W). The light power was ca.  $1.0 \text{ mW cm}^{-2}$ . The amount of generated  $\text{I}_2$  in the aqueous solution was examined from the absorption band at around 350 nm due to  $\text{I}_3^-$  measured on a UV spectrophotometer (JASCO, V-560).

### Formation of thick films by electrophoretic deposition

Particulate, thick films were formed on indium tin oxide (ITO)-coated glass substrates (40 mm × 20 mm × 1 mm) by the electrophoretic deposition using hot-water treated  $\text{SiO}_2\text{--TiO}_2$  microparticles. The microparticles

(100 mg) were dispersed in acetone (80 mL) by irradiating ultrasonic for 0.5 h.  $I_2$  (32 mg) and poly(vinylidene fluoride) (PVDF) (16 mg) were added to the colloidal suspension, and the resultant suspension was used for the electrophoretic deposition. A stainless steel spiral (SUS304BA) was used as a counter electrode. A constant voltage was applied between the two electrodes, i.e. the ITO-coated glass substrate and the stainless steel spiral, using a power supply (Model GPV 0650-0.5, Takasago), causing the electrophoresis of  $H^+$ -adsorbed, positively charged  $SiO_2$ - $TiO_2$  microparticles and the deposition on the substrate at the cathode (ITO-coated glass plate). After the electrophoresis, the substrate deposited with the microparticles was withdrawn from the suspension and dried at room temperature.

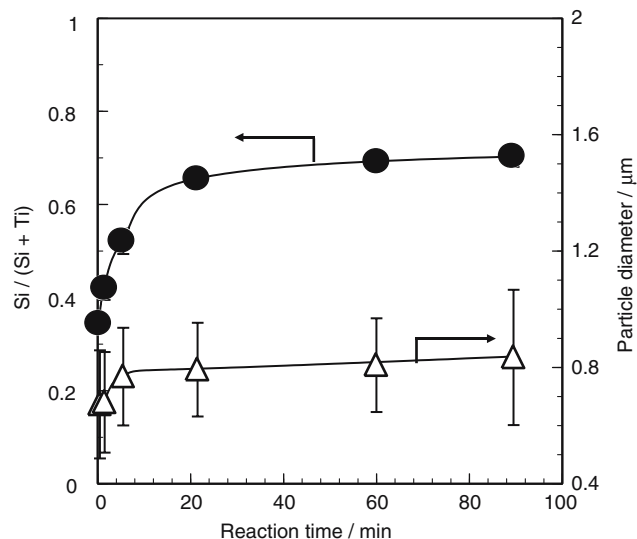
The thickness of the deposited film was estimated by cross-sectional SEM observation of the center of the film-deposited substrate. Photocatalytic activity of the film was evaluated from the photogenerated  $I_2$  in KI aqueous solutions during UV irradiation in a manner similar to that for the microparticles.

## Results and discussion

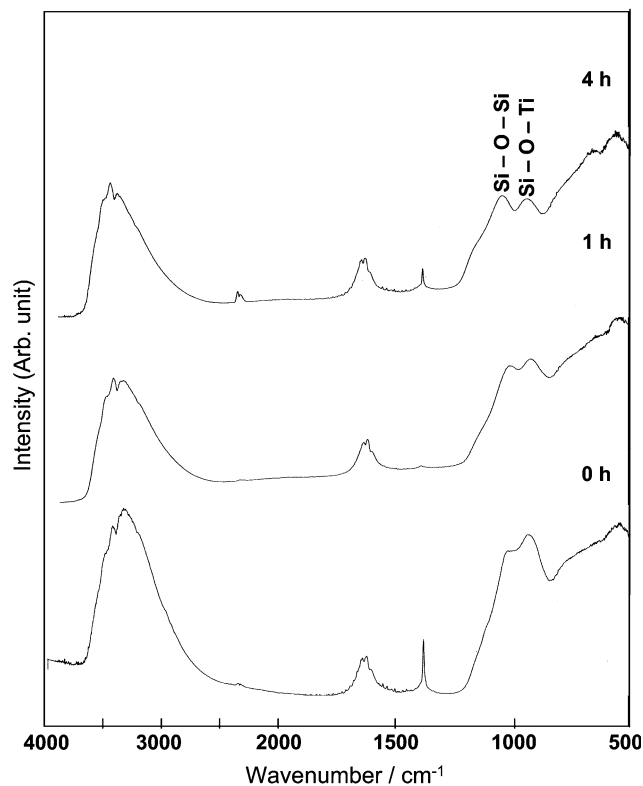
### Structure and property of hot-water treated $SiO_2$ - $TiO_2$ microparticles

The  $Si/(Si + Ti)$  atomic ratio and diameter of  $SiO_2$ - $TiO_2$  microparticles formed in the suspension as a function of copolymerization reaction time after the addition of hydrolyzed  $Si(OEt)_4$  solution are shown in Fig. 1. The atomic ratio rapidly increases in 20 min and tends to level off to 0.7, which is still smaller than that of the nominal value of 0.83. This indicates that  $TiO_2$ -rich core microparticles were firstly formed and  $SiO_2$  component was gradually introduced at the surface of the microparticles. On the other hand, the diameter of the microparticles increases with reaction time to become 0.8  $\mu m$ . The increase of diameter corresponds to the introduction of  $SiO_2$  component to the microparticles. From these results, the copolymerization reaction time for the preparation of  $SiO_2$ - $TiO_2$  microparticles in this study was fixed to 60 min.

Figure 2 shows FT-IR spectra of the  $SiO_2$ - $TiO_2$  microparticles treated with hot water at 90 °C for various times. The absorption bands at 940  $cm^{-1}$  and around at 1050  $cm^{-1}$  are assigned to Si-O-Ti bonds and Si-O bonds, respectively. The large absorption band at around 3400  $cm^{-1}$  and small band at 1600  $cm^{-1}$  are ascribed to OH bonds and  $H_2O$ , respectively. The relative intensity of the band at 940  $cm^{-1}$  due to Si-O-Ti



**Fig. 1**  $Si/(Si + Ti)$  atomic ratio and diameter of  $SiO_2$ - $TiO_2$  microparticles formed in the suspension as a function of copolymerization reaction time after the addition of hydrolyzed  $Si(OEt)_4$  solution

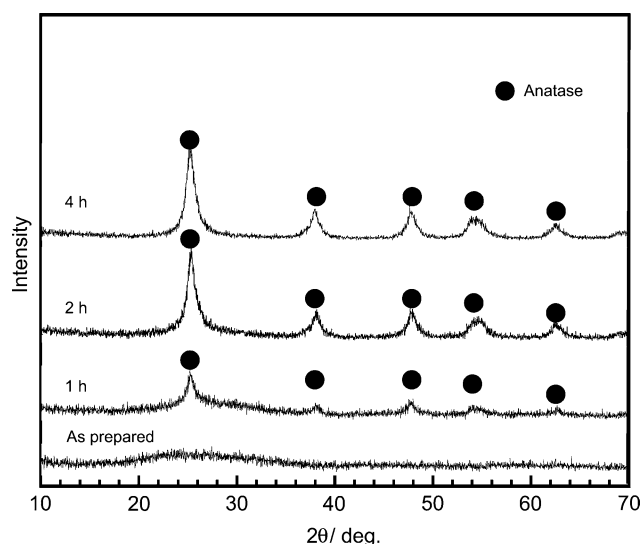


**Fig. 2** FT-IR spectra of the  $SiO_2$ - $TiO_2$  microparticles treated with hot water at 90 °C for various times

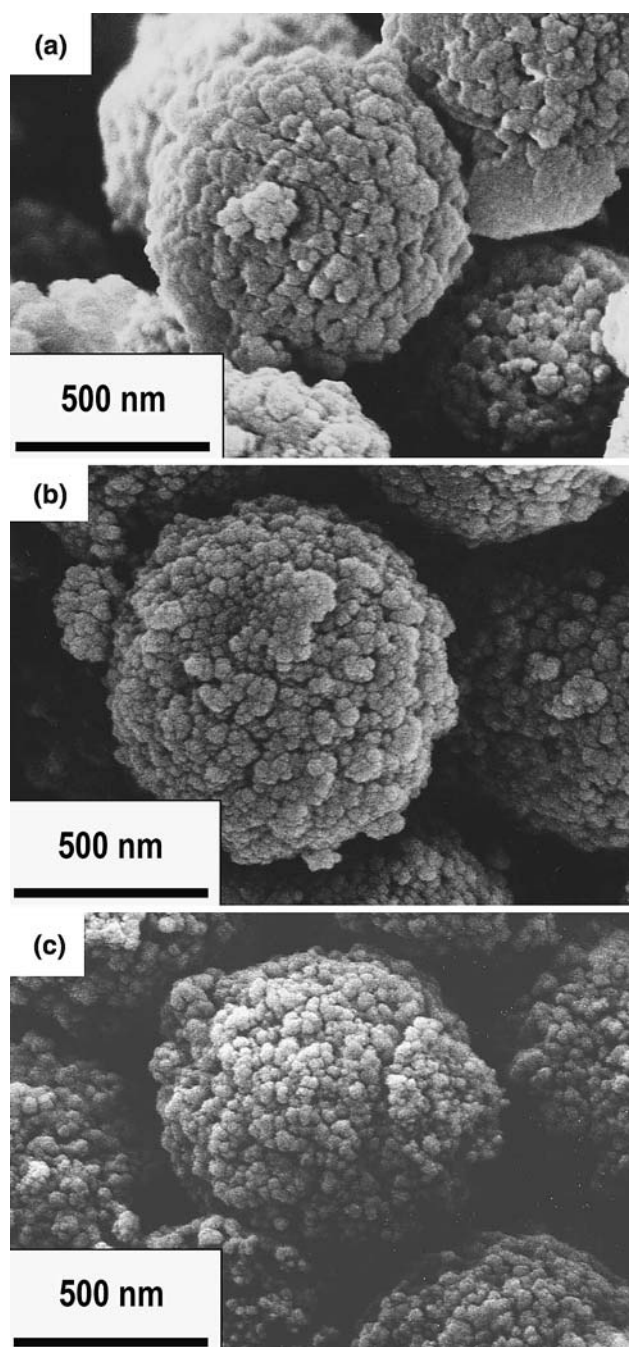
bonds decreases with the treatment, which suggests that Si-O-Ti bonds are hydrolyzed during hot-water treatment. X-ray diffraction (XRD) patterns of the

$\text{SiO}_2\text{-TiO}_2$  microparticles treated with hot water at 90 °C for various times are shown in Fig. 3. Before the hot-water treatment, the  $\text{SiO}_2\text{-TiO}_2$  microparticles are amorphous, whereas anatase is formed in the microparticles in 1 h during the treatment. It can be seen that the crystallinity of anatase improves from 1 to 2 h of the treatment and the crystallization is saturated over 2 h. These structural changes for the microparticles, i.e., hydrolysis of Si-O-Ti bonds and precipitation of anatase crystallites, are essentially the same observed for the  $\text{SiO}_2\text{-TiO}_2$  coating films on substrates during hot-water treatment as reported in the preceding literature [14, 15].

Figure 4 shows FE-SEM images of the  $\text{SiO}_2\text{-TiO}_2$  microparticles before hot-water treatment (a), after hot-water treatment for 1 h (b), and for 4 h (c). Before hot-water treatment the shape of the particles is spherical and the size is 0.7–0.8  $\mu\text{m}$ . The shape and size of the particles remain almost constant even after the hot-water treatment. It can be seen from the close-up observation that surface aggregated texture of the microparticles becomes appreciable after hot-water treatment, which should reflect the precipitation of anatase nanocrystals as indicated by the XRD patterns in Fig. 3. TEM images of the  $\text{SiO}_2\text{-TiO}_2$  microparticles treated with hot-water treatment for 4 h are shown in Fig. 5. From the low magnification observation (Fig. 5a), the  $\text{SiO}_2\text{-TiO}_2$  microparticles are found to be a secondary particle consisting of primary particles of approximately 50 nm in diameter. Crystallites with a lattice fringe of 0.35 nm corresponding to the lattice spacing of (101) in anatase are observed not only at the surface but also whole inside the microparticles (Fig. 5b).



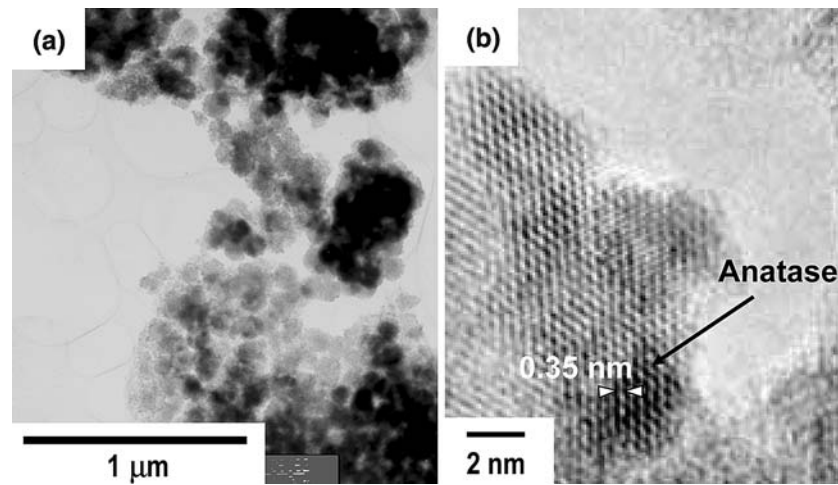
**Fig. 3** XRD patterns of the  $\text{SiO}_2\text{-TiO}_2$  microparticles treated with hot water at 90 °C for various times



**Fig. 4** FE-SEM images of the  $\text{SiO}_2\text{-TiO}_2$  microparticles before hot-water treatment (a), after hot-water treatment for 1 h (b), and for 4 h (c)

Figure 6 shows pH dependence of zeta-potential of  $\text{SiO}_2\text{-TiO}_2$  microparticles without ( $\square$ ) and with hot-water treatment for 4 h ( $\bullet$ ). The isoelectric point of the  $\text{SiO}_2\text{-TiO}_2$  microparticles without hot-water treatment is around pH 3.4, which slightly shifts to a lower value of pH 3.2 after the hot-water treatment. Isoelectric points of pure  $\text{SiO}_2$  and pure  $\text{TiO}_2$  are reported to

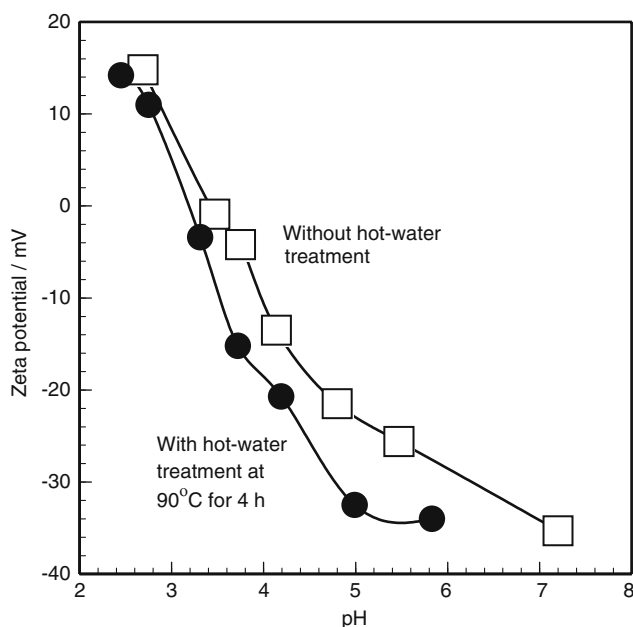
**Fig. 5** TEM images of the  $\text{SiO}_2\text{-TiO}_2$  microparticles treated with hot water treatment for 4 h



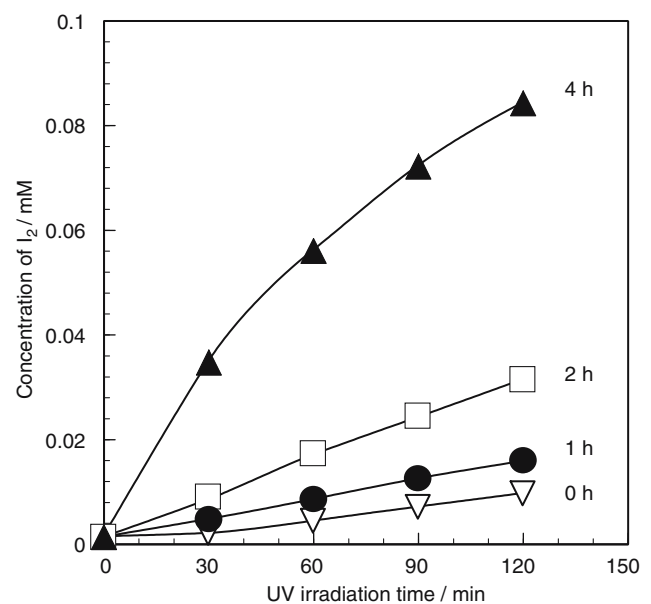
be approximately pH 2 and pH 6, respectively [29, 30]. Thus the surface property of the  $\text{SiO}_2\text{-TiO}_2$  microparticles is retained even after the formation of anatase nanocrystals in the particles by the hot-water treatment. On the other hand, specific surface area of the as-prepared  $\text{SiO}_2\text{-TiO}_2$  microparticles was  $26 \text{ m}^2 \text{ g}^{-1}$ , which remarkably increased by the hot-water treatment to be  $454 \text{ m}^2 \text{ g}^{-1}$  in 1 h and then decreased to be  $290 \text{ m}^2 \text{ g}^{-1}$  in 4 h. The changes of the surface area reflect the structural change of the microparticles such as hydrolysis of Si–O–Ti bonds and nucleation-growth of anatase nanocrystallites during hot-water treatment. Therefore, hot-water treatment for microparticles in the  $\text{SiO}_2\text{-TiO}_2$  system allows the preparation of

anatase nanocrystal-dispersed microparticles with high specific surface area, which is advantageous for high photocatalytic activity and high performance in electrodes for solar cells.

Photocatalytic activity of the  $\text{SiO}_2\text{-TiO}_2$  microparticles was evaluated from the photogenerated  $\text{I}_2$  in a KI aqueous solution during UV irradiation as shown in Fig. 7. When the hot-water treatment time for the microparticles increases, the concentration of  $\text{I}_2$  in the solution more rapidly increases with UV irradiation. This is caused by the improvement in photocatalytic activity of the microparticles due to the formation of anatase nanocrystallites. P-25 (Degussa) of pure  $\text{TiO}_2$  consisting of anatase and rutile was used as a standard



**Fig. 6** Zeta-potentials of  $\text{SiO}_2\text{-TiO}_2$  microparticles without ( $\square$ ) and with hot-water treatment for 4 h ( $\bullet$ )



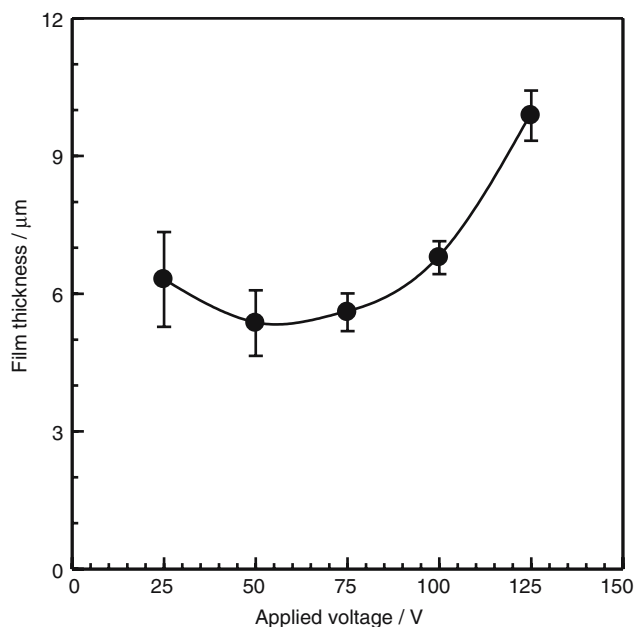
**Fig. 7** Concentration of photogenerated  $\text{I}_2$  in a KI aqueous solution due to photocatalytic activity of the  $\text{SiO}_2\text{-TiO}_2$  microparticles during UV irradiation

for comparison of photocatalytic activities. The average crystalline size and the specific surface area of P-25 are 21 nm and  $51 \text{ m}^2 \text{ g}^{-1}$ , respectively. Under the same conditions, P-25 generated  $\text{I}_2$  of 0.18 mM in 120 min, which is approximately twice that from  $\text{SiO}_2\text{-TiO}_2$  particles treated with hot water for 4 h. Taking the lower  $\text{TiO}_2$  content in the  $\text{SiO}_2\text{-TiO}_2$  particles into consideration, the hot-water treated  $\text{SiO}_2\text{-TiO}_2$  particles should have a high photocatalytic activity. The high photocatalytic activity of the hot-water treated  $\text{SiO}_2\text{-TiO}_2$  microparticles was also confirmed from the photobleaching of methylene blue in particle-dispersed aqueous solution with UV-irradiation.

#### Evaluation of electrophoretically deposited $\text{SiO}_2\text{-TiO}_2$ particulate thick films

The addition of PVDF was effective to prevent cracking of the  $\text{SiO}_2\text{-TiO}_2$  particulate, thick films, which were electrophoretically deposited. The adsorption of generated  $\text{H}^+$  from acetone and iodine on the  $\text{SiO}_2\text{-TiO}_2$  microparticles facilitated the electrophoresis to the ITO-coated glass substrate as a cathode.

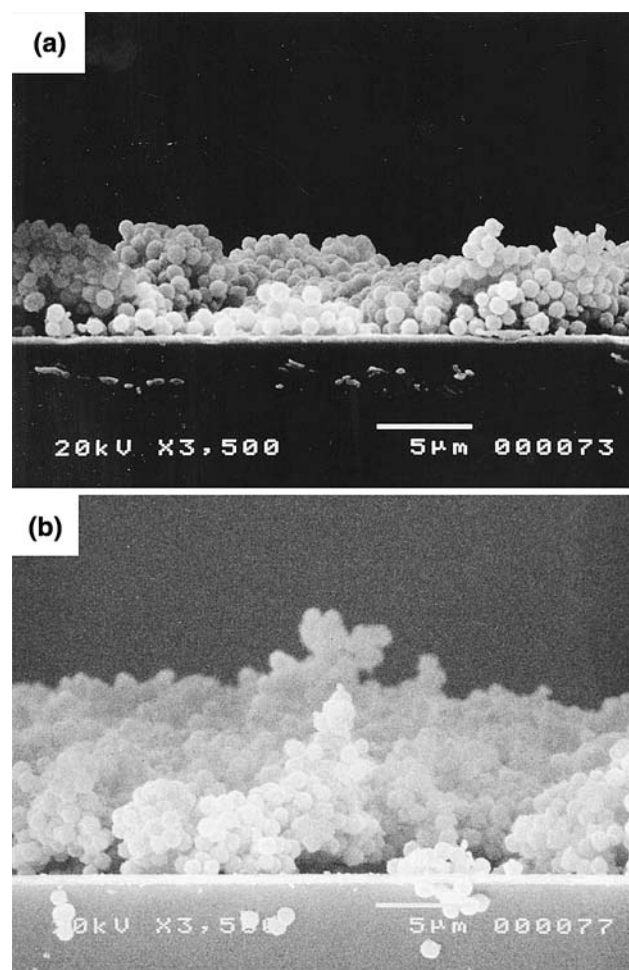
Figure 8 shows the relationship between film thickness and applied voltage. Electrophoretic deposition was carried out for 5 min at a given applied voltage. The  $\text{SiO}_2\text{-TiO}_2$  microparticles hot-water treated for 4 h were used for the deposition. The film thickness



**Fig. 8** Relationship between film thickness and applied voltage. Electrophoretic deposition was carried out for 5 min at a given applied voltage using the  $\text{SiO}_2\text{-TiO}_2$  microparticles treated with hot water for 4 h

once slightly decreased with increasing applied voltage from 25 to 50 V, and then markedly increased from 50 to 125 V to achieve 10  $\mu\text{m}$ . On the other hand, the deposition weight of the microparticles increased from 0.3 to 1.1  $\text{mg cm}^{-2}$  with increasing applied voltage from 25 to 125 V, suggesting that packing density of the deposited particles increased with the applied voltage.

Typical SEM images of cross-sections for the electrophoretically deposited particulate, thick films on ITO-coated glass substrates are shown in Fig. 9. (a) and (b) are for the films deposited for 5 min with the applied voltages of 25 and 125 V, respectively. The surfaces of both films are uneven and rugged, indicating that  $\text{SiO}_2\text{-TiO}_2$  microparticles are probably agglomerated in the suspension and the aggregates are deposited on the substrates. Further highly dispersion of the microparticles in the suspension should be



**Fig. 9** Typical SEM images of cross-sections for the electrophoretically deposited particulate, thick films on ITO-coated glass substrates; (a) and (b) were films deposited for 5 min with the applied voltages of 25 and 125 V, respectively



required to improve the packing density and the surface flatness.

Changes of  $I_2$  concentration in KI aqueous solution in a Petri dish share containing the thick film on ITO-coated glass substrate fabricated by the electrophoretic deposition of  $SiO_2$ - $TiO_2$  microparticles are shown in Fig. 10. In this case, the electrophoretic deposition was carried out at applied voltage of 100 V for 1 min using the microparticles treated with hot water for 4 h. The thickness of the film thus deposited was approximately 5  $\mu m$ . The results for the anatase nanocrystal-dispersed  $75SiO_2$ - $25TiO_2$  thin films of 0.2  $\mu m$  in thickness, which were prepared by sol-gel dip-coating and hot-water treatment at 90 °C for 5 h according to the literature [20], are shown for comparison. Electrophoretically deposited, particulate film shows much higher concentration of generated  $I_2$ , i.e. higher photocatalytic activity, than the anatase nanocrystal-dispersed  $75SiO_2$ - $25TiO_2$  coating film. The higher activity probably proves that the inside of the deposited, particulate  $SiO_2$ - $TiO_2$  film effectively acts as photocatalyst.

## Summary

Anatase nanocrystal-dispersed  $SiO_2$ - $TiO_2$  spherical microparticles were successfully prepared through sol-gel process and hot-water treatment. The formation of anatase nanocrystals proceeded through hydro-

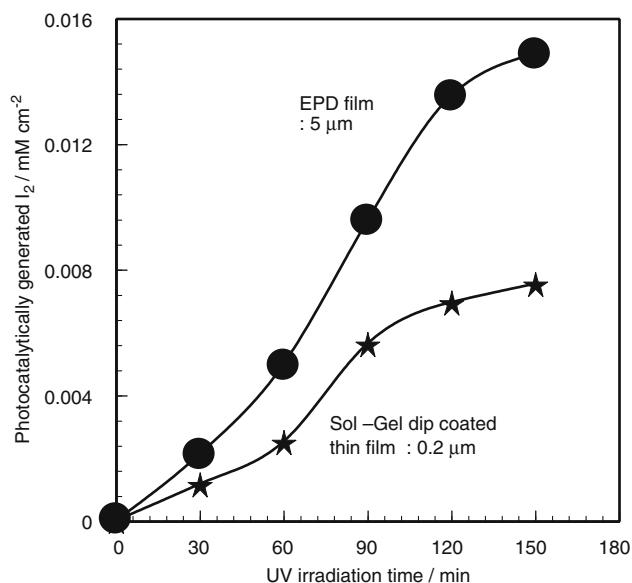
lysis of Si-O-Ti bonds, nucleation and growth at the surface as well as inside the  $SiO_2$ - $TiO_2$  microparticles. The presence of  $SiO_2$  component at the surface of the microparticles was proven by the isoelectric point. The anatase nanocrystal-dispersed spherical  $SiO_2$ - $TiO_2$  microparticles thus obtained have high specific surface area and exhibit a high photocatalytic activity.

Particulate, thick films were electrophoretically deposited on ITO-coated glass substrates using the acetone suspension containing PVDF,  $I_2$ , and anatase nanocrystal-dispersed  $SiO_2$ - $TiO_2$  microparticles. The thickness of the electrophoretically deposited particulate, thick film increased with an increase in applied voltage. High photocatalytic activity of the electrophoretically deposited particulate, thick film was confirmed from a comparison with that of the dip-coated and hot-water treated  $SiO_2$ - $TiO_2$  thin film.

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**Fig. 10** Changes of  $I_2$  concentration in KI aqueous solution in a Petri dish share containing particulate film or coating film on ITO-coated glass substrate. The thickness of the particulate film electrophoretically deposited and of the coating film dip-coated were 5 and 0.2  $\mu m$ , respectively

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