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Heat-treatment effect of dispersed particles on the preparation of thick silica films by using electrophoretic sol–gel deposition

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Thick silica films with no cracks were prepared on a stainless steel sheet by electrophoretic sol–gel deposition. The sols for electrophoresis were prepared by the re-dispersion of silica particles which were separated from the original sol made from a silicon alkoxide. The sols were then heat-treated at various temperatures in air. The heat treatment of the particles, separated by centrifugation from the original sol before the electrophoresis, prevented the generation of microcracks on the surface of the films during the drying process. The maximum thickness of the as-deposited films containing no cracks was about 10 μm when the particles were heat-treated at 600 °C for longer than 12 h.

1. Introduction

The sol–gel method is well-known as an excellent procedure to prepare thin oxide films [1, 2]. The thickness of the films prepared by conventional sol–gel methods like dip-coating is generally less than 1 μm. Some studies concerning sol–gel thick film coating have been performed, e.g. the preparation of thick silica and silica–titania films on Si substrates by repetitive spin-coating and rapid thermal annealing [3, 4]. Also thick silica coatings on soda lime glass by dip-coating in sols prepared with commercial silica particles has been reported [5]. The preparation of thick films on stainless steel sheets by conventional sol–gel methods is well known to be very difficult.

Recently we have proposed a process that combines the sol–gel method and the electrophoretic deposition method for the preparation of thick oxide films and obtained silica films on stainless steel sheets by "the electrophoretic sol–gel deposition method" [6]. These films obtained on stainless steel sheets, however, sometimes exhibited microcracks. The generation of such cracks during the drying process is attributed to the shrinkage of the particles as well as the capillary force. It is thus important to improve the properties such as surface activity and density of the silica particles in order to prepare thick films with no cracks. Heat treatment of the particles before electrophoretic deposition is expected to prevent the crack generation.

In the present study, we have prepared silica particles by the sol–gel method from silicon alkoxides, separated the particles from the sol by centrifugation, and then heated them at various temperatures in air. The particles heat-treated were re-dispersed in the mixture of ethanol and water with small amounts of methyltriethoxysilane, and deposited on the stainless steel sheets by electrophoretic sol–gel deposition. Thick silica films with no cracks were prepared on stainless steel sheets by using the heat-treated particles. In order to optimize the heat-treatment condition of the silica particles before re-dispersion for preparation of the thick silica films the influence of the heat-treatment on the silica particle density was investigated in addition to their FT–IR spectra and zeta potential.

2. Experimental procedure

2.1. Preparation and heat-treatment of silica particles

Silica particles were prepared by a procedure similar to the process developed by Stöber, Fink and Bohn (SFB process) [7] in the presence of sodium dodecyl sulphate (SDS) as a dispersant. Deionized and distilled water, distilled ethanol (EtOH) and reagent grade tetraethoxysilane (TEOS), diluted ammonium hydroxide (NH_4OH), and SDS (Wako Pure Chemical Industries, Ltd., Osaka, Japan) were used as starting materials.

SDS dissolved in 0.5 mol dm^{-3} NH_4OH solution and TEOS were diluted separately with the same amount of EtOH. The two solutions were mixed and then stirred at 25 °C for 10 h. The mole ratio of TEOS/H_2O/EtOH was fixed to be 0.2 : 10 : 10. The concentration of SDS added was 0.02 mass % against the total weight of the sols (1 kg). The particles collected by centrifugation were washed three times by a redispersion-centrifugation procedure in EtOH, and then dried in *vacuo* at room temperature for 3 h. The heat treatment of the prepared particles was carried out in air at temperatures from 400–800 °C for a period of 1–24 h.

2.2. Preparation of thick films

Fig. 1 shows the flow chart of the process from the re-dispersion of the silica particles to the electrophoretic deposition for the preparation of the thick films. The pH of the water was adjusted to be 11.7 by adding NH_4OH. The particles after heat treatment were redispersed in the mixture of H_2O ($pH = 11.7$) and EtOH by ultrasonication. Methyltriethoxysilane (MTES) (Shin-Etsu Chemical Co., Ltd., Tokyo, Japan) diluted with EtOH was mixed with the sol containing the re-dispersed silica particles and then stirred for 1 h at 25 °C. The mole ratio of $MTES/H_2O/EtOH$ was fixed to be 0.2 : 10 : 10. The amount of silica particles was 0.7 g against the total weight of the sol (70 g).

In our preliminary experiments the addition of the MTES in the preparation of the sols for electrophoresis was found to keep the films from cracking in the drying process, whereas the films deposited from the sols prepared without MTES tended to crack.

A stainless steel sheet (40 × 25 × 1 mm, SUS430) was used as a coating substrate and a stainless spiral was used as a counter electrode [6]. They were cleaned with isopropyl alcohol in an ultrasonic bath and were immersed in the sols containing the re-dispersed silica particles. The immersed surface area of the stainless steel sheet acting as an anode was 14 cm^2. A constant DC voltage was applied across the two electrodes by using a power supply (Takasago, Ltd., GPV 0650–0.5), thus causing the migration of negatively charged colloidal particles toward the anode. The voltage, the current and the number of coulombs consumed were monitored throughout the electrophoresis process by using an electronic voltmeter (TOA Dempa PM–12), an electrometer (Takeda Riken Industry TR–8651) and a coulometer (Nichia N–CR646). After the electrophoresis the coated sheets were withdrawn at a constant speed of 1.9 mm s^{-1} and dried in a desiccator over silica gel for one day. The films dried in air were heat-treated at 800 °C for 1 h after pre-heating at 400 °C for 1 h in air.

2.3. Characterization of the particles and the films

Diffuse reflectance infrared spectra of the particles were measured by a spectrometer (Perkin Elmer model 1600). The densities of the particles were determined by using a picnometer. Zeta potentials of the particles in water were measured by a laser doppler system (Malvern Zetamaster). The pH of the dispersed phase for the measurement of the zeta potentials was adjusted by adding HNO_3 or KOH.

The weight of the coated films on the stainless steel sheet was measured with a microbalance (Mettler M5SA). A scanning electron microscope (SEM) (Jeol model JSM–5300) was used for the observation of the silica particles, the surface of the deposited thick films on the stainless steel sheet, and also for the estimation of the film thickness.

3. Results and discussion

3.1. Characterization of the particles

Fig. 2 shows an SEM photograph of the silica particles separated by centrifugation from the sol and dried *in vacuo*. The mean particle size is 0.18 μm. Although the total amount of the starting materials for preparation of the particles was relatively large (1 kg), monodispersed silica particles with a small geometrical standard deviation of 1.09 were obtained.

Fig. 3 shows the FT–IR spectra of as-prepared silica particles and the particles heat-treated at various temperatures for 1 h. For all the samples a broad absorption band is observed in the range from 3000–3600 cm^{-1}. This band is associated with the O–H stretching vibrations in hydrogen-bonded molecular water and in Si–OH groups bonded to molecular water [8]. The absorption bands at around 3660 and 3746 cm^{-1} are associated with O–H stretching vibrations for hydrogen-bonded Si–OH and "free" or isolated Si–OH groups, respectively [8]. The broad band from 3000–3600 cm^{-1} in the as-prepared particles is decreased with an increase in the heat-treatment temperature and finally almost disappears at 800 °C. On the other hand, the bands due to hydrogen-bonded Si–OH and free surface Si–OH are increased up to temperatures of 600 °C. This is particularly noticeable in the case of the absorption band

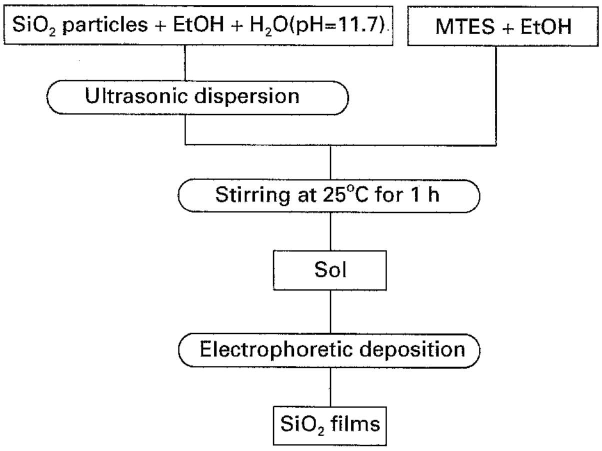

Figure 1 Thick silica film preparation process from the re-dispersion of the particles to electrophoretic deposition.

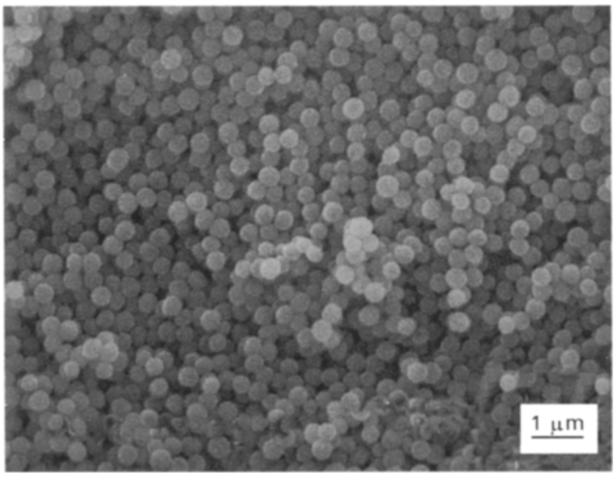

Figure 2 SEM photograph of silica particles centrifuged and dried in *vacuo* for the re-dispersion.

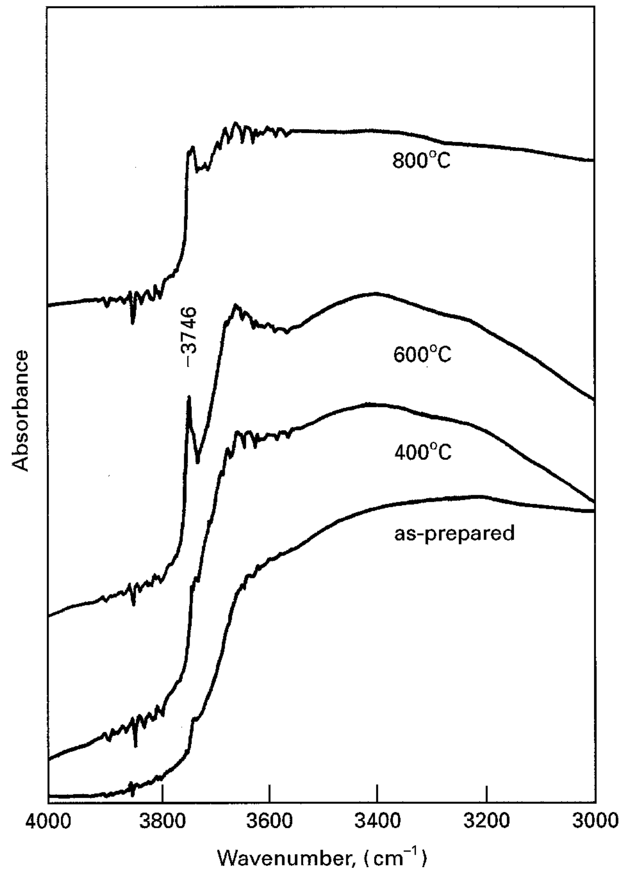

Figure 3 FT–IR spectra of silica particles heated at various temperatures for 1 h.

due to free surface Si–OH groups which become very sharp after the heat treatment at 600 °C.

Fig. 4 shows the FT–IR spectra of silica particles heat-treated at 600 °C for various heating periods. The absorption bands at 3746 and 3660 cm^{-1} are due to free Si–OH groups and hydrogen-bonded Si–OH groups respectively and are increased with increasing heating period. The broad band from 3000–3600 cm^{-1} arising from the presence of molecular water is decreased. When the heating period is longer than 12 h, the intensity of the absorption band due to free Si–OH groups becomes saturated.

Fig. 5 shows the density of the particles heated at a fixed heating temperature of 600 °C for various periods of time. The density of the as-prepared particles, 1.8 $g\,cm^{-3}$, is close to that of silica particles prepared by the conventional SFB process, which was reported to be 1.9 $g\,cm^{-3}$ [9]. The density of the silica particles is increased with increasing heating period and saturates at 12 h, approaching the density (2.2 $g\,cm^{-3}$) of fused silica [10].

Fig. 6 shows the zeta potentials of the as-prepared silica particles and the particles heat-treated at 400 °C for 1 h, 600 °C for 1 and 12 h. The isoelectric points (IEP) of the particles are around 3 in all cases. When the pH is larger than the IEP, the negative values of the zeta potential of the particles are increased from 0 to − 70 mV as the pH value increases from 3 to 12. It is noteworthy that the zeta potentials are almost the same value for any heating condition at a given pH value, indicating that the heating condition does not affect the charge of the particles.

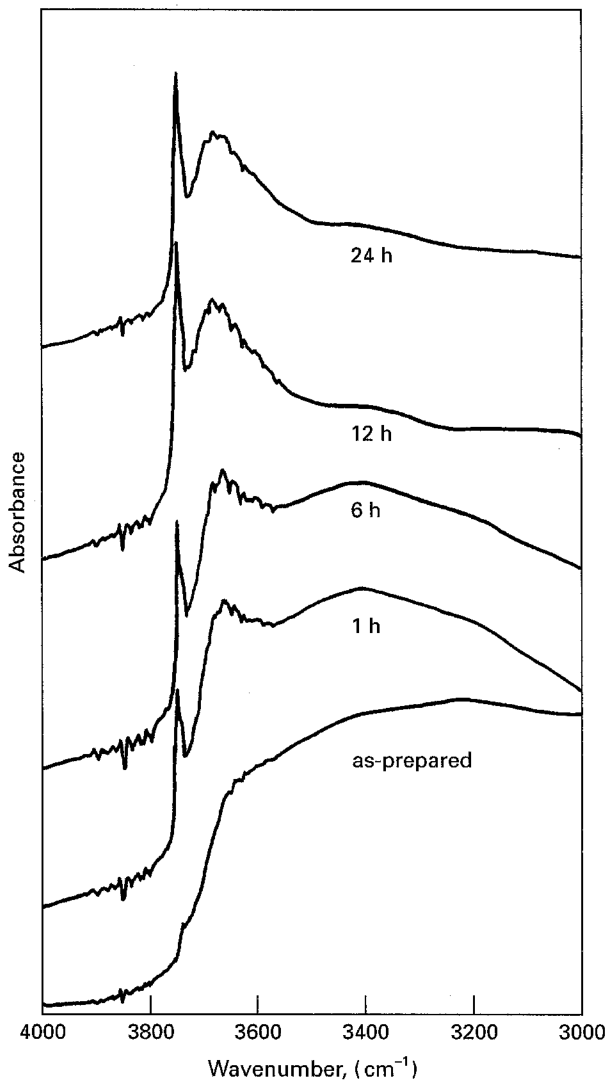

Figure 4 FT–IR spectra of silica particles heated at 600 °C for different periods.

Attempts were made to re-disperse the silica particles heat-treated under various conditions in a mixture of the same mole ratio of H_2O (pH = 11.7) and EtOH by ultrasonication. The re-dispersibility of the particles in the dispersal medium for the electrophoresis is shown in Table I. When the heating temperature of the particles is lower than 600 °C, good re-dispersibility of the particles is obtained. However, particles heated at 800 °C for 1 h were aggregated and could not be re-dispersed by ultrasonication.

It is thus concluded that silica particles with high density, good re-dispersibility properties and surfaces rich in free Si–OH groups are obtained by heating at 600 °C for 12 h as a pre-treatment for electrophoresis.

3.2. Preparation of thick films

For electrophoretic deposition, we used particles heated at temperatures lower than 600 °C since as discussed previously particles aggregate when heated at higher temperatures.

Fig. 7 shows the weights of the silica films prepared by electrophoretic deposition of the particles on stainless steel sheets as a function of applied voltage for 5 min. The deposited weight, which is increased with

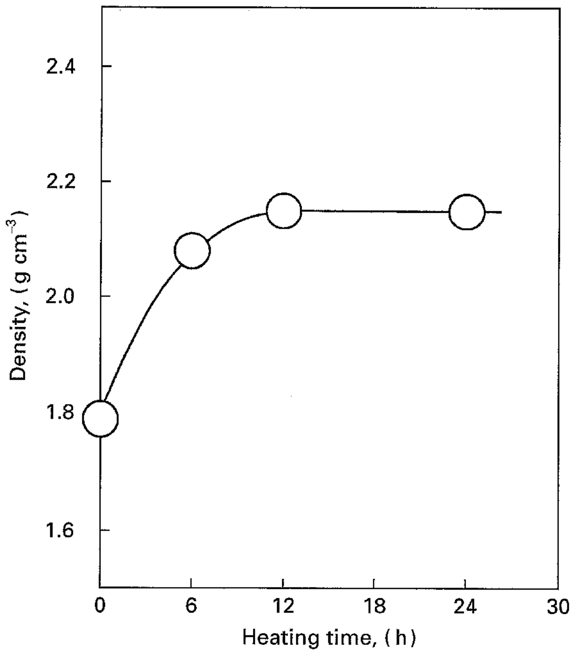

Figure 5 Density of silica particles as a function of heating period. Heating temperature was fixed at 600 °C.

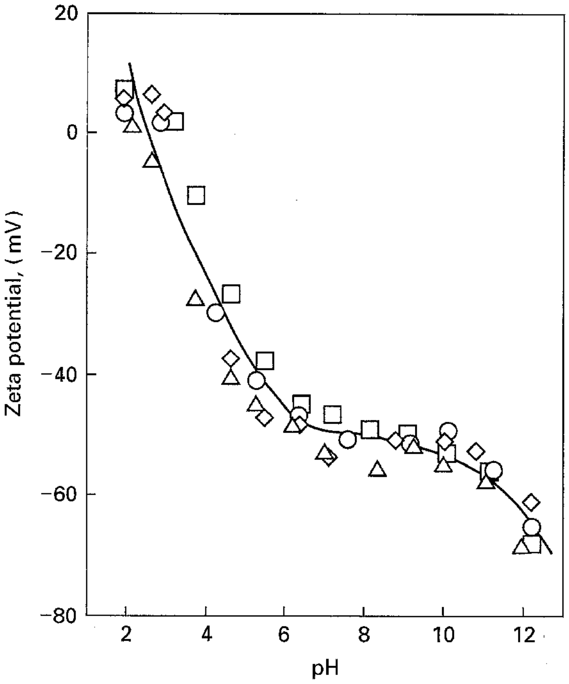

Figure 6 Zeta potentials of the particles heated under various conditions. (△): as prepared, (□) 400 °C 1 h, (◇) 600 °C 1 h and (○) 600 °C 12 h.

TABLE I Re-dispersibility of the particles heated at various conditions (○; good, ×; bad)

Heating condition of silica particles	Dispersibility in the mixture of H_2O (pH = 11.7) and EtOH
as-prepared	○
400 °C, 1 h	○
600 °C, 1 h	○
600 °C, 12 h	○
600 °C, 24 h	○
800 °C, 1 h	×

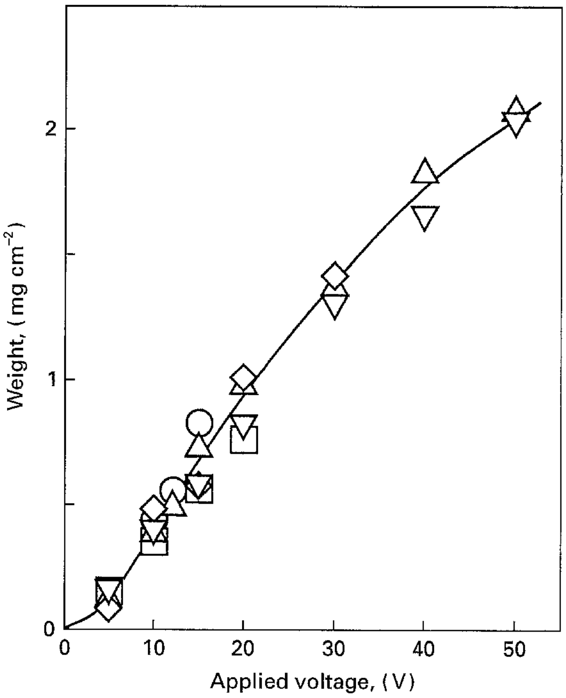

Figure 7 Weights of silica films deposited on stainless steel sheets by using the particles heated under various conditions. (○): as prepared, (□) 400 °C 1 h, (◇) 600 °C 1 h, (△) 600 °C 12 h, and (▽) 600 °C 24 h.

increasing voltage, is basically not influenced by the heating condition of the particles. This is evidenced by the point that the deposited weight was mainly governed by the charge of the particles and the zeta potential of the particles and these properties are not influenced by the heating condition as is shown in Fig. 6.

On the other hand, the adhesion of the deposited film was influenced by the heating conditions. All the films prepared from particles with no heat treatment peeled off in the drying process when the applied voltage was larger than 20 V. However, the films did not peel off, and also exhibited no cracks after drying, when the particles were heat-treated at 600 °C for 12 and 24 h and the applied voltage was smaller than 60 V. When the applied voltage was larger than 60 V, the edges of the films peeled off during the electrophoresis mainly due to the generation of large amounts of O_2 gas from the surface of the coating sheet.

The heat-treatment effect of the silica particles on the prevention of crack generation in deposited films was evaluated in terms of the maximum thickness of the films that could be produced without cracks. Table II lists the heating conditions of the particles before re-dispersion and the corresponding maximum thickness of the as-deposited films containing no cracks. In order to evaluate the maximum thickness of the films, the amount of deposition by electrophoresis was varied by using a different applied voltage with a fixed deposition time of 5 min. The films with thickness of 5, 7 and 10 μm in Table II were prepared by applying voltages of 20, 30 and 50 V, respectively. Crack generation was confirmed by SEM observation. Cracks were observed for all the films prepared from the

TABLE II Maximum thickness of the as-deposited films with no cracks prepared from the particles heated under various conditions

Heating condition of silica particles	Maximum thickness (µm)
400 °C, 1 h	5
600 °C, 1 h	7
600 °C, 12 h	10
600 °C, 24 h	10

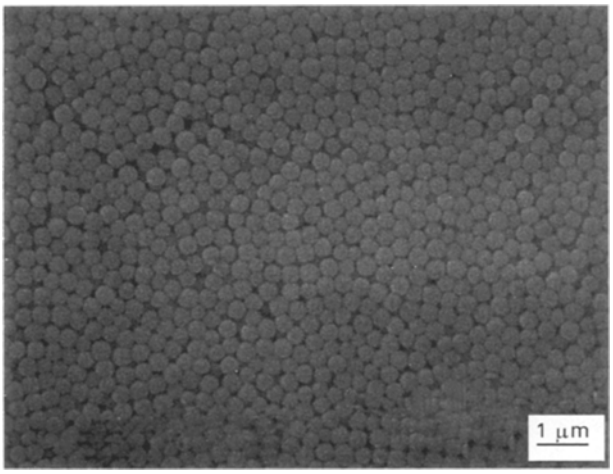

Figure 8 SEM photograph of the surface of the thick film after heat treatment.

particles with no heat treatment. However, when heat treatment of the particles before re-dispersion was carried out, crack-free films were prepared by electrophoretic sol–gel deposition. The maximum thickness of the films with no cracks was increased with increasing the heating temperature and period. When the heating period was longer than 12 h at 600 °C, the thickness of the films was about 10 µm. The generation of cracks on the surface of the films is mainly caused by the shrinkage of the particles swelled by the re-dispersion in the basic solutions. The extent of the swelling of the particles became smaller when the heating temperature was higher. This is because rigid Si–O–Si networks in the particles were developed by the heat treatment at higher temperatures. In this way, thick silica films with no cracks after drying were prepared by using particles heat-treated at 600 °C for 12 h that showed a high density and a good re-dispersibility.

3.3. Heat treatment of the film

Heat treatment of the films prepared by electrophoretic sol–gel deposition of the particles heat-treated at 600 °C for 12 h on a stainless steel sheet was carried out at 800 °C for 1 h in air after pre-heating at 400 °C for 1 h in air. Fig. 8 shows the surface structure of the heat-treated film on the stainless steel sheet. The applied voltage for the electrophoresis was 10 V and the period was 10 min. The thickness of the film was ∼4 µm. As shown in Fig. 8a, crack free film was prepared. Although the as-deposited films were easily peeled off by scratching, the films heat-treated at 800 °C strongly adhered to the stainless steel sheet.

4. Conclusions

In the formation of thick silica films by electrophoretic sol–gel deposition of re-dispersed silica particles the heat treatment of the particles prepared by the sol–gel process prevented films from cracking during the drying process. With an increase in the heat treatment temperature and the heating period of the particles for re-dispersion, the maximum thickness of the crack free films was increased. When the particles were heated at 600 °C for longer than 12 h, as-deposited thick silica films of ∼ 10 µm in thickness with no cracks were prepared by electrophoretic sol–gel deposition.

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