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## **Deposition of thick, rigid and size-controlled silica particle layer on aluminum sheet for water vapor adsorption**

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### **ABSTRACT**

Toward the development of a new adsorbent heat exchanger of adsorption chillers, silica-coated aluminum sheets were prepared by the combination of sol-gel and electrophoretic deposition techniques. Silica sols were synthesized by the hydrolysis of tetraethoxysilane precursor in an ethanol solution, and then a silica layer was directly formed on an aluminum sheet by electrophoretic deposition of the silica sols. The silica-coated aluminum sheets were subjected to the aging treatment in an ammonia water bath with a DC electric field. This aging treatment was found to be very effective to form rigid silica layer on aluminum sheet. It was found that the obtained layer was composed of monodisperse and spherical submicron-sized silica particles. Sodium dodecyl sulfate (SDS) in the silica sol solution played an important role in controlling the deposited amount of silica particles as well as their sizes. The particle size increased from 0.10 to 0.83  $\mu\text{m}$  with an increase in SDS concentration. For the silica-coated aluminum sheet prepared at a pH value of 10.6 and a SDS concentration of 0.05 mass%, the deposited amount reached a maximum value of 19.8  $\text{mg cm}^{-2}$ , which was much higher than those reported by Kishida *et al.* (1994). The prepared composites were evaluated for the characteristics of water vapor adsorption through volumetric experiments. The results of adsorption experiments showed that the composite with a higher silica content adsorbed a larger amount of water vapor in the relative pressure range below 0.3.

**Keywords:** Silica-coated aluminum sheet, Sol-gel process, Electrophoretic deposition, Water vapor adsorption, Adsorption cooling

## Nomenclature

$D_{p50}$	mean particle diameter [ $\mu\text{m}$ ]
$m$	coated mass of silica [ $\text{mg cm}^{-2}$ ]
$q$	amount adsorbed [ $\text{kg kg}^{-1}$ ]
$R$	silica content in composite [%]

## Greek symbols

$\varphi$	relative pressure [-]
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## 1. Introduction

Adsorption heat pumps and chillers are heat transformation systems, by which low-temperature industrial waste heat and solar energy are converted to the state with a higher energy-saving potential [1-3]. Adsorption chillers with silica gel/water or synthetic zeolite/water pairs have been in practical use, but the usage is still limited because they are large, heavy and expensive when compared to liquid absorption chillers or vapor compression systems [4,5]. The adsorption chillers generally consist of a solid adsorbent-heat exchanger (Ad-HEX), evaporator and condenser units, and the conventional Ad-HEX units have an adsorbent particle bed with a poor thermal conductance. Therefore, the specific cooling performance (SCP) of adsorption chiller is determined by the heat transfer rate in the Ad-HEX. The introduction of many heat exchange metal plates in the adsorbent bed for an increase in SCP leads to the growth in size of Ad-HEX unit. In order to reduce the size, heat exchange plates were coated with adsorbent particles by the aid of binders [6,7] or the adsorbent thin layers were synthesized directly on the plates [8,9].

Silica gel is one of the potential adsorbent candidates for adsorption chiller because of its high adsorption capacity of water vapor, readiness in desorption at a relatively-low temperature and cost effectiveness. Kishida *et al.* [10] proposed an interesting method for coating metal substrates with silica particles without any binders. In this method, silica sols were prepared through the conventional sol-gel process and the silica particles were migrated to a metal substrate by electrophoresis to form the silica particle layer on the substrate. They conducted the electrophoretic silica coating on a pure aluminum, anodized aluminum and stainless-steel sheets, and examined the effects of the preparation conditions on the formation of silica particle layer [10-15]. Silica-coated aluminum sheets are the most suitable for the Ad-HEX unit, since aluminum has a high thermal conductance. Kishida *et al.* [10] reported that the anodized aluminum substrate was coated with a larger amount of silica compared to the aluminum substrate, but the coated amount was only  $4.8 \text{ mg cm}^{-2}$ , which was too small to apply to the Ad-HEX for water vapor adsorption, and therefore they did not investigate the adsorption properties of water vapor.

In the present study, in order to increase the coated mass of silica particles on aluminum sheet we

revised the conditions of sol-gel process and electrophoretic deposition process, namely the pH value of silica-sol solution, DC voltage applied, processing time and temperature. Furthermore, an aging treatment in an ammonia water bath with an applied electric field was newly introduced after the formation of silica particle layer on the aluminum sheet. The prepared silica-aluminum composites were characterized in term of the coating property, such as the amount of silica and the particle size, and also the water vapor adsorption capacity was evaluated.

## 2. Experimental

The preparation procedure of silica-coated aluminum sheets proposed in the present work consisted of four processes; silica sol preparation, electrophoretic deposition, aging and drying as shown in Fig. 1. Silica sol preparation and electrophoretic deposition were carried out by referring to the procedures proposed by Kishida *et al.* [10] and Nishimori *et al.* [11]. Silica sols were obtained by a base-catalyzed hydrolysis of tetraethoxysilane (TEOS). The solution of TEOS, ethanol and deionized water were prepared at a molar ratio of 0.2 : 10 : 10, and various amounts of sodium dodecyl sulfate (SDS) were added to the mixed solution. The solution pH, which was measured by a pH meter (HM-30G, DKK-TOA Co., Japan), was varied by the addition of ammonia water. The solution was subjected to the agitation for 1 h at 25°C. The reagents used in the present work; TEOS, ethanol, SDS and ammonia water were all purchased from NACALAI TESQUE, INC., Japan.

An aluminum sheet with a purity of 99.7% was used as a substrate for silica coating. The sheet was 65 mm long, 18 mm wide and 0.3 mm thick. In order to remove grease, naturally oxidized film and other contaminants on the surfaces of the aluminum sheet, the sheet was chemically pretreated as follows. The aluminum sheet was soaked with an 8 vol% sulfuric acid aqueous solution of 20°C for 7 min. After washing the sheet with distilled water, it was etched with a 60 g L<sup>-1</sup> aqueous sodium hydroxide of 45°C for 5 min. After washing it with water again, the sheet was immersed in 5 vol% sulfuric acid aqueous solution of 20°C for 5 min. The sheet was rinsed again with distilled water [16].

During the electrophoretic deposition of silica particles, the aluminum sheet was an anode in the silica-sol solution to deposit negatively charged silica particles onto the surface. 27 mm from the bottom on both sides of the sheet was the active surface for the electrophoretic deposition by insulating the other parts of the sheet using a masking plastic tape. A stainless steel sheet (SS304), 50 mm long, 18 mm wide and 2 mm thick, was used as a cathode. The distance between the electrodes was 15 mm. Constant DC voltage was applied to the electrodes using a power supply (EX-375H2, Takasago Ltd., Japan). During the electrophoretic deposition of silica particles, the silica particles migrate toward the aluminum sheet and gradually form silica gel particles on the aluminum surface.

The silica-coated aluminum sheet was taken out from the silica-sol solution and set as an anode in an ammonia water of pH 10.7. Then, aging treatment for completing the gelatification was carried out with applying a DC voltage of 200 V for 5 h. Only the samples obtained by the prolonged and/or high-

temperature electrophoresis were subjected to the aging treatment at 100 V for 5 h in ammonia water of pH 9.0 in order to prevent the silica particle layer from local destruction. Finally, the sample sheet was subjected to preliminary drying at room temperature for 24 h and main drying at 150°C for 24 h.

The amount of silica particles deposited on the aluminum sheet was determined by the difference in mass before the electrophoretic deposition and after the two-step drying. The diameter of silica particles was determined from a scanning electron microscope (SEM) image of the surface of silica-coated aluminum sheet. Silica-aluminum composites were evaluated for the water vapor adsorption properties by using a volumetric measuring apparatus [17].

### **3. Results and Discussion**

#### **3.1 Aging treatment**

The aging treatment was carried out after the electrophoretic deposition prior to the drying in order to complete the gelatification in a basic solution and prevent the detachment of the deposited silica particles from the aluminum sheet. Fig. 2 demonstrates the effectiveness of aging treatment. The upper two pictures in Fig. 2 show the surfaces of silica-coated aluminum sheets after drying with and without the aging treatment, and the bottom two pictures are the SEM images of the cross-section of silica particle layers. The electrophoretic deposition was conducted at 200 V for 10 min in silica-sol solution of pH 11.6 without SDS. We confirmed that the maximum coated amount of silica on aluminum sheet was obtained at an electrophoresis voltage of 200 V as shown in Fig. SM-1 (Supplementary Material). The aging was performed on the silica-coated aluminum sheet in an ammonia water of pH 10.7 with applying a DC voltage of 200 V. As seen in the upper pictures of Fig. 2, the aging treatment is effective to produce a homogeneous silica film without cracks on the aluminum sheet. The particle layer with the aging treatment is rigid and adhesive to the aluminum sheet so that it cannot be easily peeled by scratching with fingers. On the other hand, for the sample without the aging the silica film is partially peeled off from the surface of aluminum sheet during the drying process (upper right picture of Fig. 2). The samples prepared by the electrophoretic silica coating at different pH values also showed the similar film detachment during the dry process without the aging treatment. It is very interesting to see in the bottom left picture that silica particles reside in the dents of aluminum surface which may be created during the aging process because DC electric voltage applied during the aging compressed the silica particles on the aluminum surface. The large contact area between the silica particles and aluminum substrate causes the strong adhesion of silica particles onto the substrate. Additionally, siloxane bonds may be formed between silica particles by the dehydration of hydroxyl groups.

Since the aging treatment is proved to be effective to create a rigid and adhesive silica particle layer, the aging treatment was conducted as a routine for the fabrication of silica gel-aluminum composites in the present work.

### 3.2 Electrophoretic silica coating

Silica-coated aluminum sheets were prepared by electrophoresis using silica sol solutions with different pH values and additive amounts of SDS. The electrophoretic deposition was carried out under fixed conditions: the applied DC voltage of 200 V, processing time of 10 min and bath temperature of 25°C. Fig. 3 shows the effects of the solution pH and SDS concentration on the coated mass of silica on aluminum sheet,  $m$ . The SDS concentration in silica-sol solution was defined as the amount of SDS per unit mass of silica sol. The pH value of silica-sol solution was measured before the electrophoretic deposition was started. We confirmed that there were not significant changes in pH value before and after this process. As seen from Fig. 3, the coated mass of silica strongly depends on both pH and SDS concentration. In the SDS-free solution, the coated amount is smaller than that in the solution with SDS, and its maximum value is ca. 5.0 mg cm<sup>-2</sup>. Fig. 4 shows the mean diameter of silica particles deposited on aluminum sheet as a function of pH for the silica-sol solution with and without SDS. Error bars in this figure represent the standard deviations of silica particle sizes. The mean particle diameter in either case increases with the solution pH due to the base catalysis of ammonia water on the hydrolysis of TEOS. The dependence of the silica particle size on pH for the SDS-free solution is stronger than that for the solution that contains SDS. At the same pH, silica particles with larger sizes are deposited on aluminum sheet by using silica-sol solution with SDS, indicating that SDS promotes the formation of large silica particles in the sol-gel process. The similar effect was reported by Nishimori *et al.* [11]. Therefore, the addition of SDS in the initial stage of silica sol preparation is of advantage to precipitating more silica particles on aluminum sheet in the electrophoretic process.

The initial concentration of SDS has a major effect on the electrophoretic silica coating as shown in Fig. 3. The coated mass of silica on aluminum sheet in either SDS concentration varies markedly with pH and has the maximum value at a given pH. The pH corresponding to the maximum amount shifts to the lower value with increasing SDS concentration. In the range of SDS concentration studied in this work (0.025–0.150 mass%), the largest amount of silica coating is obtained at a SDS concentration of 0.050 mass%, and the maximum value reaches 19.5 mg cm<sup>-2</sup> at pH = 10.6. Meanwhile, for the silica-coated aluminum sheets prepared using silica-sol solutions containing SDS of 0.050 mass% at pH 11.0–11.6, the coating thickness, which was measured by a micrometer, ranged from 60 to 150 μm and the layer densities from 180 to 360 mg cm<sup>-3</sup>.

Fig. 5 shows the SEM images of silica particles deposited on aluminum sheet by electrophoresis using the solution with different additive amounts of SDS at around a pH of 10.6. The mean particle diameters are described in this figure. The silica particle size clearly increases with the SDS concentration. As described above, the formation of larger silica particles leads to the larger amount of coating, but the larger particles are simultaneously hard to migrate in the solution due to large fluid resistance and gravitational sedimentation. Actually we confirmed the precipitation of silica particles at the bottom of the bath after 10-min electrophoretic deposition. Furthermore, the addition of SDS

results in an increase in ionic strength of the silica-sol solution. SDS provides the silica-sol solution with sodium ion, thereby causing a reduction in the surface charge of silica particles. Hence, excessive addition of SDS has an adverse effect on the deposition of silica particles.

The coated mass of silica on aluminum sheet is also significantly affected by the electrophoretic deposition time and temperature. The prolonged and/or high-temperature electrophoresis leads to the larger amount of coating as shown in Figs. SM-2 and SM-3 (Supplementary Material). However, the excessively thick silica layer on aluminum sheet was found to become somewhat fragile.

### 3.3 Water vapor sorption

Fig. 6 shows the adsorption isotherms of water vapor on the four silica-coated aluminum composites with different silica contents at 30°C. The composite with a 13-wt% silica was prepared using a silica-sol solution without SDS, and the other composites using a silica-sol solution containing SDS of 0.050 mass% under different conditions. The ordinate of this figure is the equilibrium uptake of water vapor per unit mass of the composite and the abscissa is the relative pressure, which is defined as the ratio of the water vapor pressure in equilibrium to the saturated vapor pressure at the adsorption temperature. A water-vapor adsorption cooling takes place in the range of relative pressure below 0.29 under the conditions: evaporation temperature of 10°C, cooling temperature of 30°C and generation temperature of 80°C. As seen from Fig.6, all the prepared composites have water-vapor adsorption capacities. The amount adsorbed increases with an increase in relative pressure, and the composite with a higher silica content adsorbs a larger amount of water vapor at a given relative pressure. In the adsorption isotherms based on the water uptake per unit mass of silica in the composite, which is shown in Fig. SM-4 (Supplementary Material), the amounts of adsorption show almost the same values regardless of the silica content. These results indicate that the deposited silica particles have similar pore structures. The water-vapor adsorption capacity of the silica-coated aluminum composite is determined mainly by the amount of silica deposited on aluminum surface. However, the amounts adsorbed on the deposited silica particles are lower than that on a commercial silica gel (RD2560, Fuji Silysia Chem. Ltd, Japan). The improvement in adsorption capacity of silica particle on aluminum sheet will be needed for a practical use.

## 4. Conclusions

Silica-coated aluminum sheets were prepared as a new composite material for water adsorption chiller with a combination of sol-gel and electrophoretic deposition processes. Silica sols were synthesized from tetraethoxysilane under the basic conditions, and then a silica layer was directly formed on an aluminum sheet by electrophoretic deposition of the silica sols. The aging treatment in an ammonia water bath with a DC electric field was newly introduced after the electrophoretic deposition. This aging treatment was found to be very effective to form rigid silica layer on the

aluminum sheet. The obtained layer was composed of monodispersed and spherical submicron-sized silica particles. The SDS added to the silica sol solution played an important role in controlling the deposited amount of silica particles and their sizes. The particle size increased from 0.10 to 0.83  $\mu\text{m}$  with an increase in SDS concentration. For the silica-coated aluminum sheet prepared at a pH value of 10.6 and a SDS concentration of 0.05 mass%, the deposited amount reached a maximum value of 19.8  $\text{mg cm}^{-2}$ . The results of adsorption experiments showed that the composite with a higher silica content adsorbed a larger amount of water vapor in the relative pressure range below 0.3.

### Acknowledgments

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## Figure captions

Fig. 1. Illustration of coating process of aluminum sheet with silica particles.

Fig. 2. Photographs of silica-coated aluminum sheets and SEM images of the cross-section of silica particle layers, (a) with aging treatment and (b) without aging treatment.

Fig. 3. Effect of pH of silica-sol solution and additive amount of SDS on coated mass of silica.

Fig. 4. Relationships between mean diameter of silica particles and pH of silica-sol solution with and without SDS.

Fig. 5. SEM images of silica particles on aluminum sheet prepared at different SDS additive amounts, (a) 0.025 mass%, pH = 10.7, (b) 0.050 mass%, pH = 10.6, (c) 0.100 mass%, pH = 10.6, (d) 0.150 mass%, pH = 10.6.

Fig. 6. Adsorption isotherms of water vapor on silica-coated aluminum composites at 30°C.

## Figures

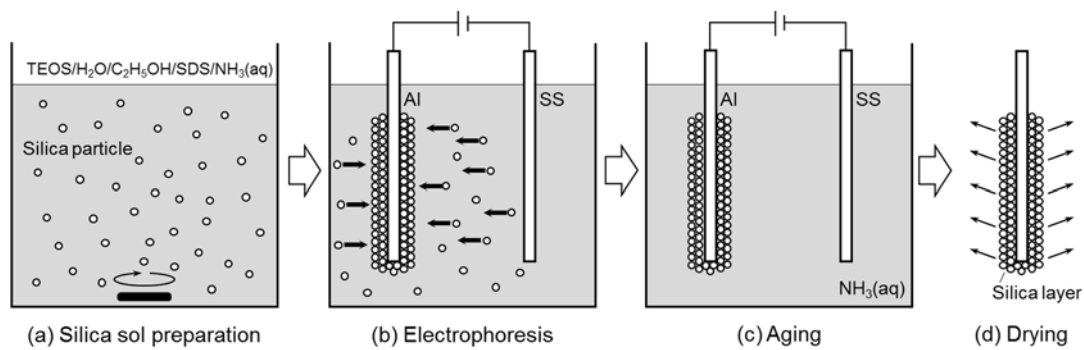


Fig. 1. Illustration of coating process of aluminum sheet with silica particles.

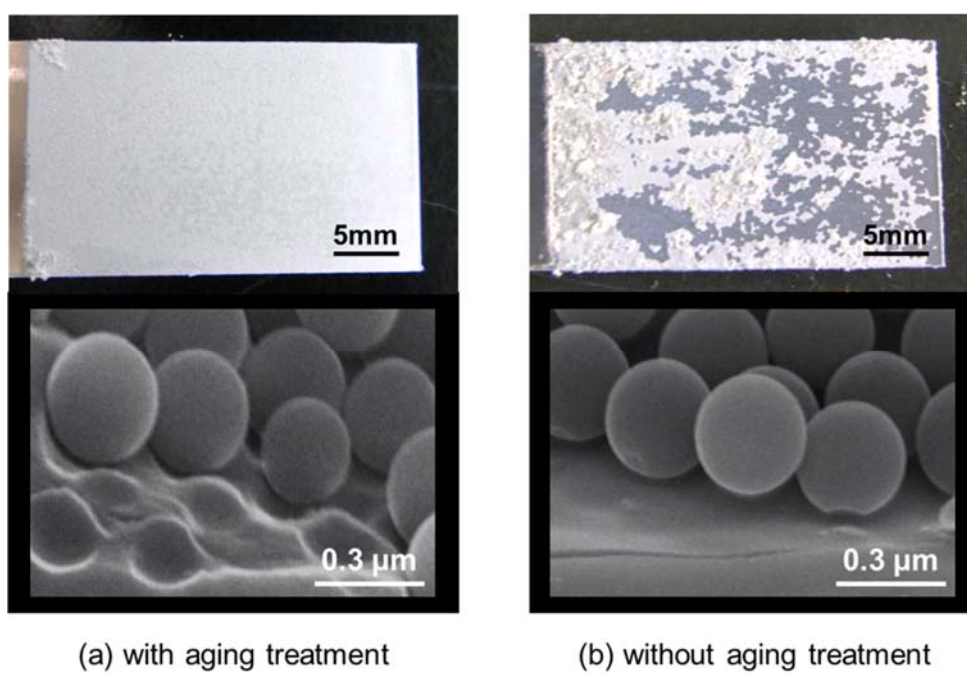


Fig. 2. Photographs of silica-coated aluminum sheets and SEM images of the cross-section of silica particle layers, (a) with aging treatment and (b) without aging treatment.

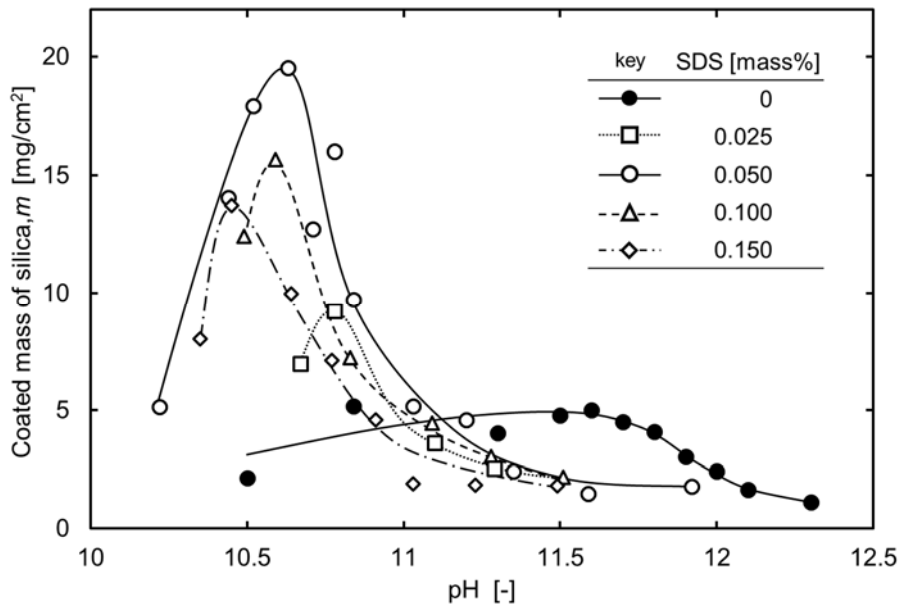


Fig. 3. Effect of pH of silica-sol solution and additive amount of SDS on coated mass of silica.

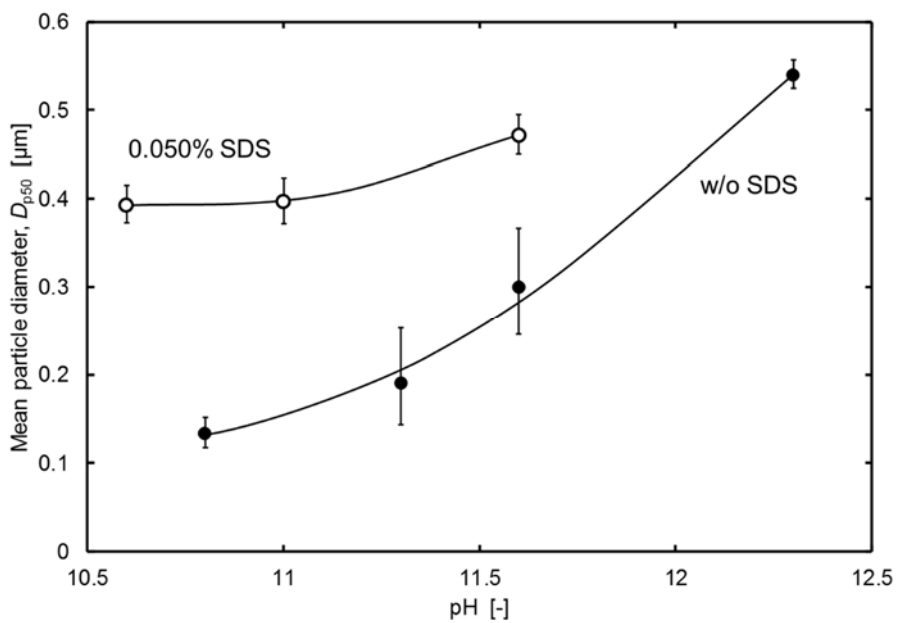


Fig.4. Relationships between mean diameter of silica particles and pH of silica-sol solution with and without SDS.

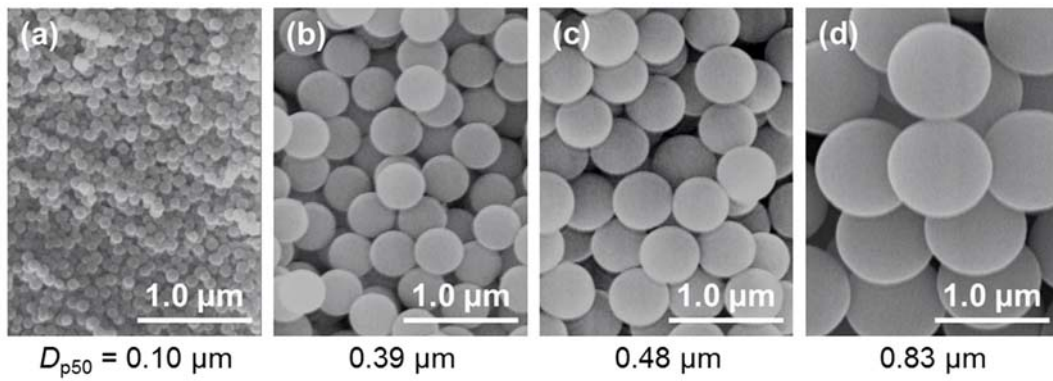


Fig.5. SEM images of silica particles on aluminum sheet prepared at different SDS additive amounts, (a) 0.025 mass%, pH = 10.7, (b) 0.050 mass%, pH = 10.6, (c) 0.100 mass%, pH = 10.6, (d) 0.150 mass%, pH = 10.6.

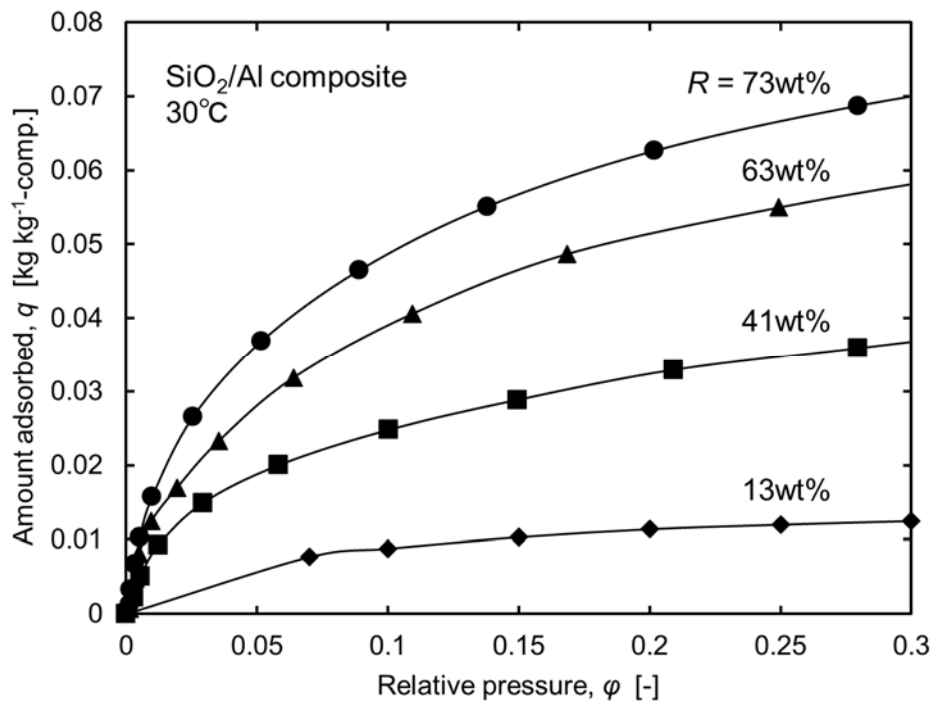
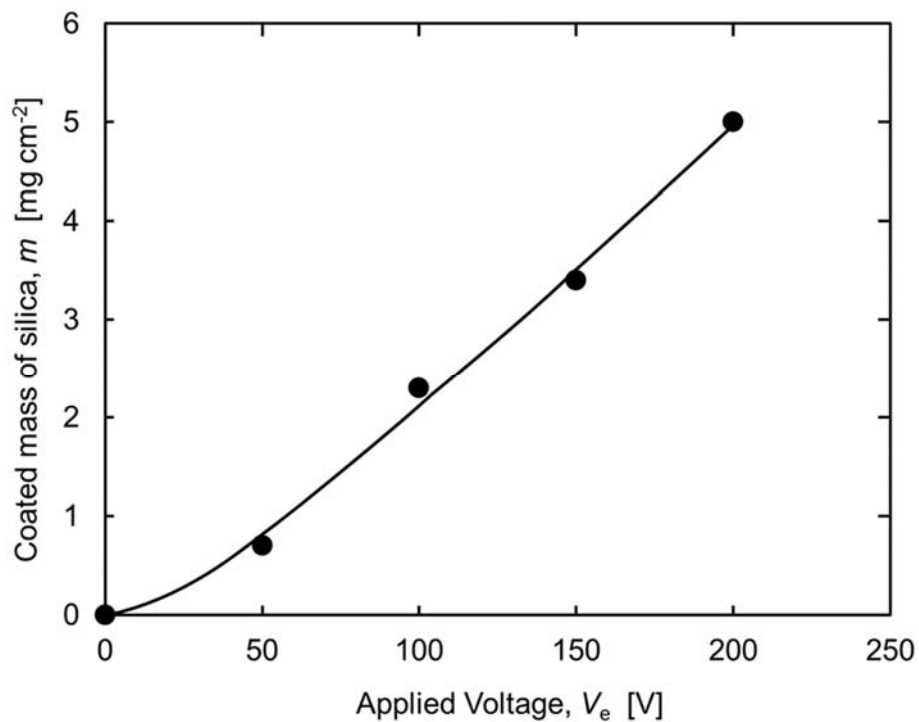
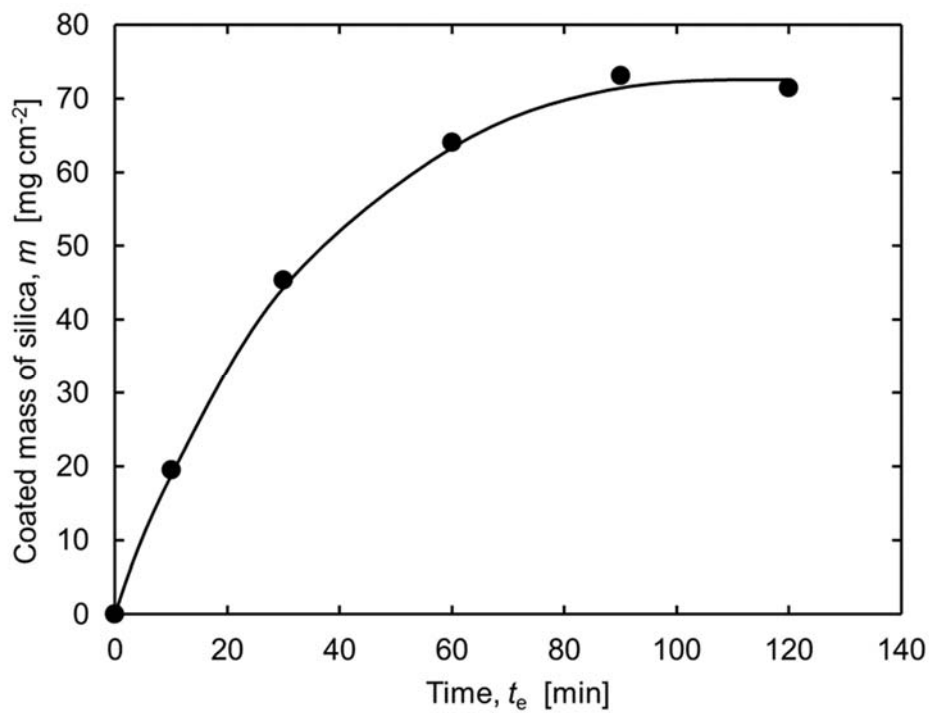


Fig. 6. Adsorption isotherms of water vapor on silica-coated aluminum composites at 30°C.

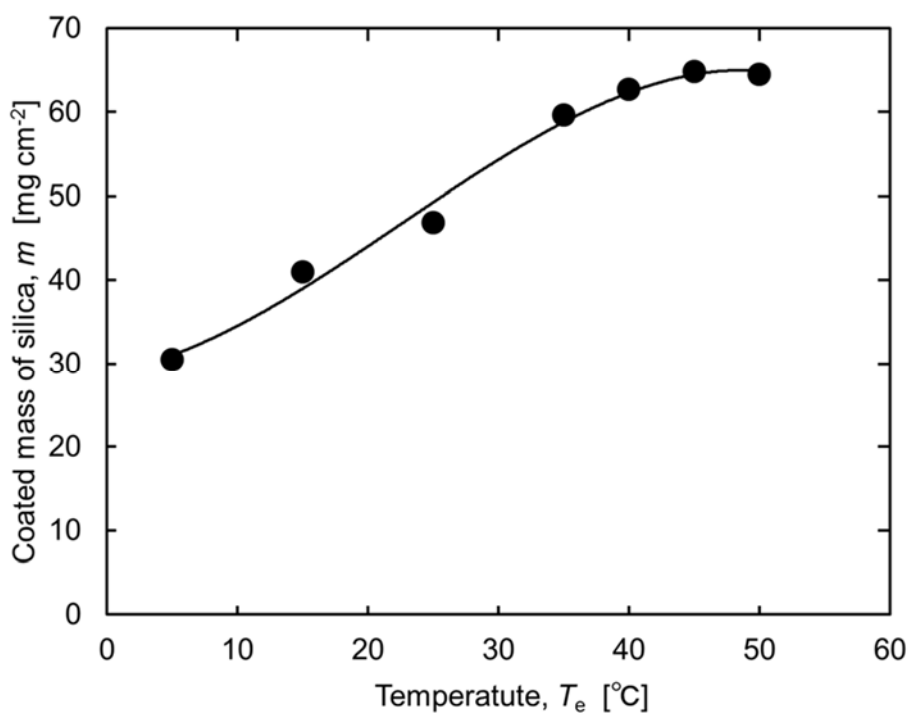
### Supplementary Material



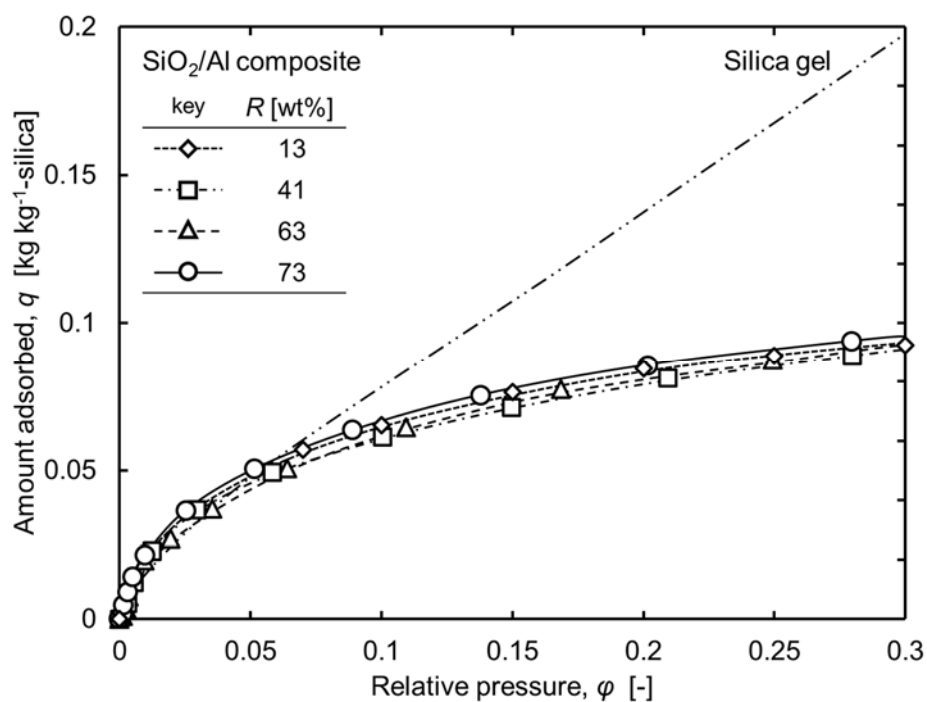
**Fig. SM-1** Effect of applied DC voltage on coated mass of silica on aluminum for 10-min electrophoretic deposition using silica-sol solution of pH 11.6 without SDS.



**Fig. SM-2** Effect of electrophoretic deposition time on coated mass of silica on aluminum (silica-sol solution of pH 10.6 with SDS of 0.05 mass%,  $V_e = 200$  V,  $T_e = 25^\circ\text{C}$ ; aging treatment at 100 V for 5 h in ammonia water of pH 9.0).



**Fig. SM-3** Effect of temperature of electrophoresis bath on coated mass of silica on aluminum (silica-sol solution of pH 10.6 with SDS of 0.05 mass%,  $V_e = 200$  V,  $t_e = 30$  min; aging treatment at 100 V for 5 h in ammonia water of pH 9.0).



**Fig. SM-4** Adsorption isotherms of water vapor on silica-coated aluminum composites and silica gel (RD2560, Fuji Silysia Chem. Ltd) at 30°C.