

## Adsorption of Colloidal Silica Particles on a Glass Substrate

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### ABSTRACT

Colloidal particles of silica (100 nm in size) were electrostatically dispersed and adsorbed on a glass substrate coated with silica sol or alumina sol. Stability of the suspensions and microstructure of the adsorbed particle layers were discussed in terms of total potential energies between the particles and the substrate. Well-dispersed suspension resulted in a layer with densely packed and regularly arranged particles, whereas less stable suspension resulted in a porous layer with loosely packed and irregularly arranged particles. Despite repulsive interactions between the particles and the substrate coated with silica sol, the observed adsorption can be attributed to chemical bonds formed at the interface between the particle and silica sol. In contrast, the adsorption of the particles on the substrate coated with alumina sol formed a layer with strongly adhered and densely packed particles, due to large attractive interactions between the particles and alumina sol.

**Key words :** Silica, Adsorption, Stability, Total potential energy

### 1. Introduction

Adsorption of colloidal particles in an aqueous solution on the surface of solid is an important phenomenon in many processes for forming and coating of ceramics. A variety of dense, solid layers or bodies of ceramics have been prepared by electrophoretic deposition of charged particles.<sup>1)</sup> Recently, with a growing interest in nanoscale powders, a great deal of research has been done on dispersion, rheology and consolidation behavior of suspensions consisting of nanoparticles and larger, submicrometer or micrometer particles.<sup>2-5)</sup>

The adsorption occurs when an attractive force due to electrostatic interactions between oppositely charged particles and substrate exists. The adsorption depends on the magnitudes and relative sign of the charges developed on particles and substrates in an electrolyte solution. Additionally, there are other factors affecting the adsorption such as chemical bonds between particles and substrates, hydration force and thermal motion of particles.<sup>6)</sup> The theoretical treatment of the particle adsorption has been made in terms of total potential energy resulting from interactions between particles and substrates.<sup>6,7)</sup>

Microstructure of a layer of colloidal particles adsorbed on a substrate may be related to the dispersion of particles in a suspension. According to Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, the stability of particles containing electrical double layers is governed by the height of a poten-

tial energy barrier. A high potential barrier provides a dominant repulsion between particles and results in a stable suspension where particles are uniformly dispersed. If the potential barrier is too low or no barrier exists, the suspension becomes unstable due to flocculation of particles. Therefore, the adsorption of well-dispersed particles can form a layer with a regular arrangement of particles, whereas the adsorption of flocculated particles can form a layer with an irregular arrangement of particles.

In the present study, monodispersed spherical particles of silica (100 nm in size) were prepared as model colloidal particles in order to investigate the relationship between the stability of the particles in suspensions and the arrangement of the particles adsorbed on the substrate. The particles were electrostatically dispersed and adsorbed on the glass substrate coated with silica sol or alumina sol. The microstructure of the adsorbed particle layer was discussed in terms of total potential energies between the particles and between the particles and the substrate.

### 2. Experimental Procedure

Spherical particles of silica were prepared by Stöber method.<sup>8)</sup> TEOS (0.3 mol/L ethanol, Acros, USA, 98%) diluted in ethanol (99.9%, Hayman Ltd., UK) was added to a mixture of H<sub>2</sub>O (0.6 mol/L ethanol) and NH<sub>4</sub>OH solution (20 ml/L ethanol) and stirred until hydrolysis reaction was completed. The particles were separated by repeating centrifuge and decantation of the suspensions and then dried at 100°C for 24 h under vacuum. The dried particles were electrostatically dispersed in water by adjusting pH with 0.1 M HNO<sub>3</sub> and 0.1 M NH<sub>4</sub>OH solutions. The suspensions at pH 3, 4, 6, 8 and 8.6 were prepared and the final content of sil-

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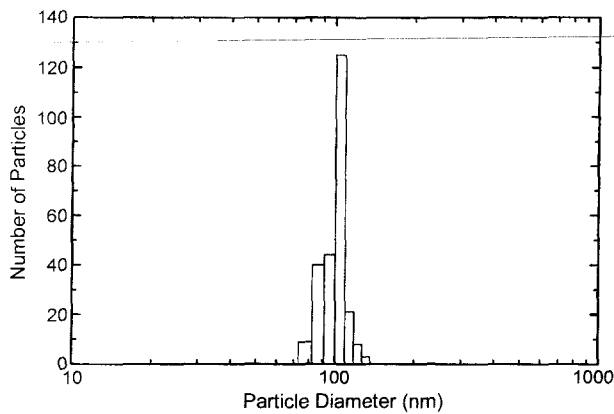


Fig. 1. Particle size distribution of silica determined from SEM micrographs.

ica was fixed to 1.5 wt%.

Size distribution of the silica particles was measured with SEM (JSM-5410, JEOL, Japan). Using SEM photographs and a digitizing tablet, 250 particle diameters were measured and the result is shown in Fig. 1. The particles with an average diameter of 100 nm show nearly monosized distribution and their sizes range from 80 nm to 127 nm.

Electrophoretic mobilities of the particles in the suspensions were measured with a zeta potential analyzer (Zeta-Plus, BI Corp., USA) and the zeta potentials were calculated using the Henry equation:<sup>9)</sup>

$$\zeta = \frac{3\mu_e\eta}{2\varepsilon_0\varepsilon_r} \cdot \frac{1}{f(\kappa R)} \quad (1)$$

where  $\mu_e$  is electrophoretic mobility ( $\text{m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ ),  $\eta$  is viscosity of water (25°C,  $0.8937 \times 10^{-3} \text{ Pa} \cdot \text{s}$ ),  $\varepsilon_0$  is the dielectric permittivity of vacuum ( $8.85 \times 10^{-12} \text{ F/m}$ ),  $\varepsilon_r$  is the relative dielectric constant of water (25°C, 78.54),  $\kappa$  is the Debye-Hückel parameter ( $\text{m}^{-1}$ ) and  $R$  is the radius of particle (m). The value for  $f(\kappa R)$  was taken from Smith's data.<sup>10)</sup>

Adsorption of the silica particles was carried out by dip-coating. Micro cover glass, which had been cleaned with acetone and 1 N HCl solution, was immersed into the suspension for 10~20 s and then slowly withdrawn upward. The excess particles on the substrate were rinsed off by flowing the supernatant obtained from centrifuging the suspension over the substrate. The substrate was dried at room temperature and microstructure of the adsorbed particle layer was observed with SEM.

The substrate was coated with silica sol or alumina sol prior to dip-coating. For the substrate without sol coating, most particles were removed from the substrate during the washing step regardless of the suspension pH. The silica sol was used in most experiments and the alumina sol was used in the suspension of pH 6. The silica sol was prepared by dropwise addition of a mixture of water (14.4 ml), ethanol (22 ml) and HCl solution into a mixture of TEOS (44.5 ml) and ethanol (22.5 ml). The molar ratio of  $\text{H}_2\text{O}$  to TEOS was 4 and pH was adjusted to 1.6. The alumina sol was pre-

pared by adding 117.8 ml of aluminum secondary butoxide ( $\text{Al}(\text{O-sec-C}_3\text{H}_7)_3$ , Aldrich, USA) to 832.2 ml of  $\text{H}_2\text{O}$  at 85°C and peptizing with  $\text{HNO}_3$  solution.

### 3. Results and Discussion

In order to calculate the zeta potential of the silica particle from the electrophoretic mobility, the value of  $\kappa R$  should be known. The Debye-Hückel parameter can be obtained as follows:<sup>9)</sup>

$$\kappa = \left( \frac{1000e^2 N_A}{\varepsilon_0 \varepsilon_r k_B T} \sum_i Z_i^2 M_i \right) \quad (2)$$

where  $e$  is the charge of electron,  $N_A$  is the Avogadro number,  $\varepsilon_0$  is the dielectric permittivity of vacuum,  $\varepsilon_r$  is the relative dielectric constant of water,  $k_B$  is the Boltzmann constant,  $T$  is absolute temperature,  $Z_i$  is the valence of  $i$  ion and  $M_i$  is the concentration of  $i$  ion (mol/L).

In this study, no electrolyte other than  $\text{HNO}_3$  and  $\text{NH}_4\text{OH}$  was added to adjust the pH of the suspension. Because the amount of  $\text{HNO}_3$  or  $\text{NH}_4\text{OH}$  was not measured during the experiments, it was estimated that the electrolyte concentrations in the suspensions of pH 3.0~8.6 were no more than  $1.0 \times 10^{-3} \text{ M}$ . Based on the electrolyte concentrations, the value of  $\kappa R$  ( $\kappa = 1.04 \times 10^8 \text{ m}^{-1}$ ,  $R = 5 \times 10^{-8} \text{ m}$ ) was found to be 5.2, which is beyond the limit of the application of the Smoluchowski equation ( $\kappa R > 100$ ) or the Hückel equation ( $\kappa R < 0.1$ ) for the zeta potential.<sup>9)</sup> Thus, the zeta potentials with respect to the suspension pH were calculated with the Henry equation and the results are shown in Fig. 2.

The silica particles are negatively charged at pH above the isoelectric point (3.4), as shown in Fig. 2. The zeta potential increases with increasing pH, because the adsorption of  $\text{OH}^-$  ions on the particle surface is strongly dependent on pH. The zeta potentials cannot be directly compared with the values in the literature since the zeta potentials of silica particles vary with the presence of impurity and preparation methods. The zeta potentials of the particles were ~1.3 times larger than those obtained with the Smolu-

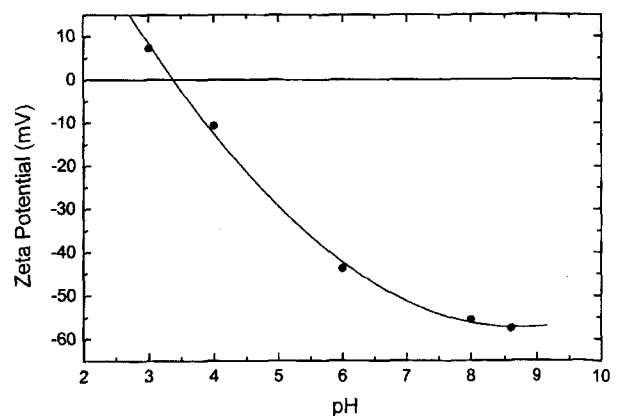


Fig. 2. Zeta potential as a function of suspension pH calculated using Henry eq.

chowski equation.<sup>4,11)</sup> However, the zeta potentials between pH 6–8.6 was found to differ in  $\pm 5\%$  for silica particles which were synthesized by the same method as in this study.<sup>12)</sup>

The stability of the silica suspension depends on total interparticle potential energy. Total potential energy is the sum of the attractive potential energy resulting from long-range van der Waals interactions between the particles and the repulsive potential energy due to electrical double layer interactions. When the distance ( $s$ ) between two spherical particles with radii  $R_1$  and  $R_2 < 25$  nm, the attractive potential energy can be approximated as

$$V_A(s) = -\frac{A_{12}}{6} \left[ \frac{2R_1R_2}{s^2 + 2R_1s + 2R_2s} + \frac{2R_1R_2}{s^2 + 2R_1s + 2R_2s + 4R_1R_2} + \ln \left( \frac{s^2 + 2R_1s + 2R_2s}{s^2 + 2R_1s + 2R_2s + 4R_1R_2} \right) \right] \quad (3)$$

where  $A_{12}$  is the Hamaker constant between two particles in an aqueous medium.<sup>9)</sup> The repulsive potential energy can be approximated from the zeta potentials ( $\zeta_1, \zeta_2$ ) instead of surface potentials of two particles using the solution of the linearized Poisson-boltzmann equation:<sup>13)</sup>

$$V_R(s) = \frac{\pi\epsilon_0\epsilon_r R_1R_2}{R_1 + R_2} [(\zeta_1 + \zeta_2)^2 \ln(1 + e^{-\kappa s}) + (\zeta_1 - \zeta_2)^2 \ln(1 - e^{-\kappa s})] \quad (4)$$

The DLVO plots of calculated total potential energies for the silica particles are shown in Fig. 3, where  $R_1=R_2=50 \times 10^{-9}$  m,  $A_{12}=0.46 \times 10^{-20}$  J<sup>14)</sup> and the zeta potentials ( $\zeta_1=\zeta_2$ ) were taken from Fig. 2. The repulsive potential energy due to interactions between two electrical double layers is proportional to the zeta potential which changes with pH. As a result, a maximum in the total potential energy, i.e., a potential barrier, increases with pH. According to the

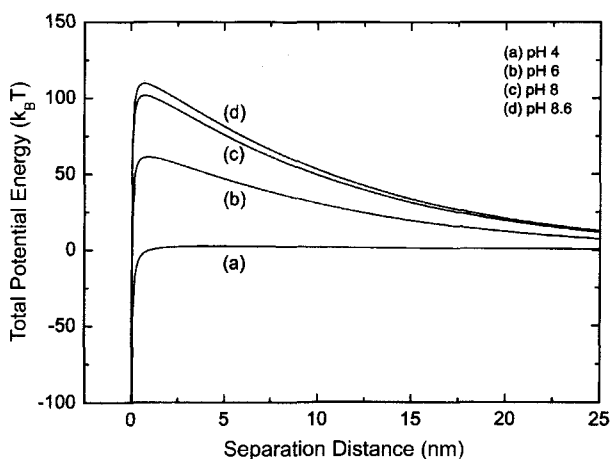


Fig. 3. DLVO plots of total potential energies between silica particles as a function of separation distance: (a) pH 4 ( $\zeta=-10.6$  mV), (b) pH 6 ( $\zeta=-43.7$  mV), (c) pH 8 ( $\zeta=-55.5$  mV) and (d) pH 8.6 ( $\zeta=-57.5$  mV).

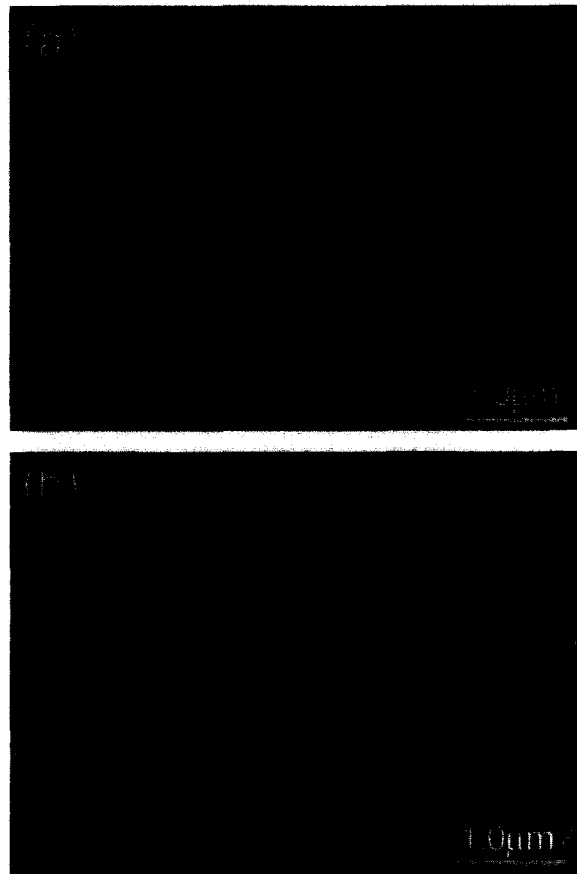


Fig. 4. SEM micrographs of silica particles adsorbed on the substrate coated with silica sol: suspensions at (a) pH 6 and (b) pH 8.

DLVO plots in Fig. 3, the suspensions at pH 6, 8 and 8.6 are stable, since the potential barriers ( $>61 k_B T$ ) are much higher than thermal energy of the particles ( $\sim 10 k_B T$ ). The suspension at pH 8.6 is most stable and the particles are well dispersed. At pH 4 near the isoelectric point, the interaction between the particles is essentially attractive, indicating that the particles are unstable against flocculation.

Fig. 4(a) and (b) show the arrangement of the particles adsorbed by dipping the substrates coated with silica sol in the suspensions at pH 6 and 8, respectively. The adsorbed layer obtained from the suspension at pH 6, as shown in Fig. 4(a), consists of loosely packed and irregularly arranged particles. The layer appears to be multiple and excess silica sol is seen between the particles. On the other hand, the adsorbed layer obtained from the suspension at pH 8, as shown in Fig. 4(b), consists of clusters with approximately 60 particles, which are uniformly packed in a hexagonal or cubic array. In addition, there are cracks running through boundaries, where mismatch in the regular arrangement of the particles occurs. These cracks are attributed to stress developed throughout the layer during drying of the substrate.

Fig. 5 exhibits the arrangement of the particles obtained

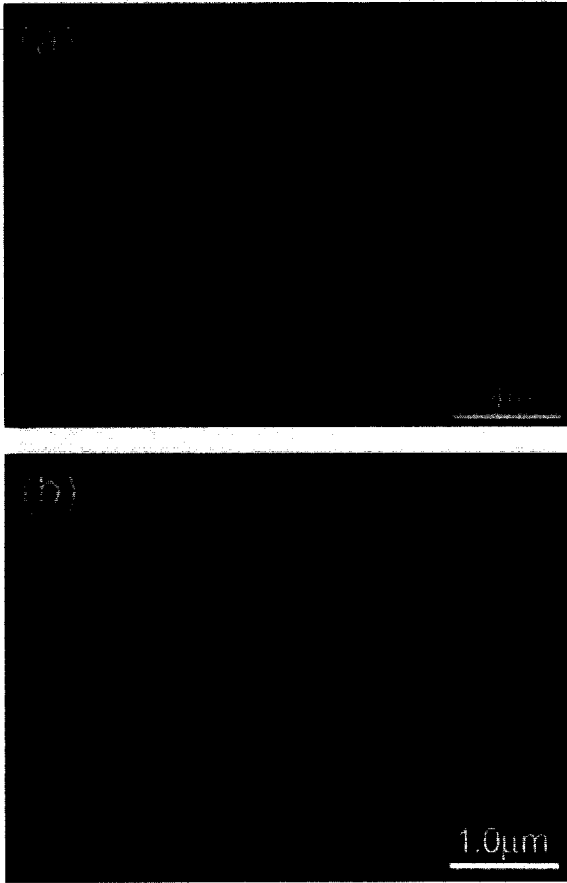


Fig. 5. SEM micrographs of silica particles adsorbed on the substrate coated with silica sol: suspension at pH 8.6.

from the suspension at pH 8.6. The adsorbed particles are densely packed in a hexagonal array and result in a dense, crack- and pore-free monolayer, as shown in Fig. 5(b). The smooth, thin layer with incomplete coverage of the particles is seen in low magnification (Fig. 5(a)).

An attempt to explain the adsorption and arrangement of the silica particles was made in terms of total potential energy due to the interaction between the particles and the substrate. By setting the radius of one particle ( $R_2$ ) to  $\infty$  in equations (3) and (4), the attractive potential energy can be written as<sup>15)</sup>

$$V_A(s) = -\frac{A_{12}}{6} \left[ \frac{2R_1(s+R_1)}{s(s+2R_1)} + \ln\left(\frac{s}{s+2R_1}\right) \right] \quad (5)$$

and the repulsive potential energy can be expressed as

$$V_R(s) = \pi\epsilon_0\epsilon_r R_1 [(\zeta_1 + \zeta_2)^2 \ln(1 + e^{-\kappa s}) + (\zeta_1 - \zeta_2)^2 \ln(1 - e^{-\kappa s})] \quad (6)$$

Fig. 6 shows the DLVO plots for the silica particles and the substrate coated with silica sol as a function of separation distance ( $s$ ) between the particle and the substrate. The Hamaker constant ( $A_{12}$ ), the zeta potentials ( $\zeta_1 = \zeta_2$ ) and  $\kappa$  were taken from the values in Fig. 3. The DLVO plot for the

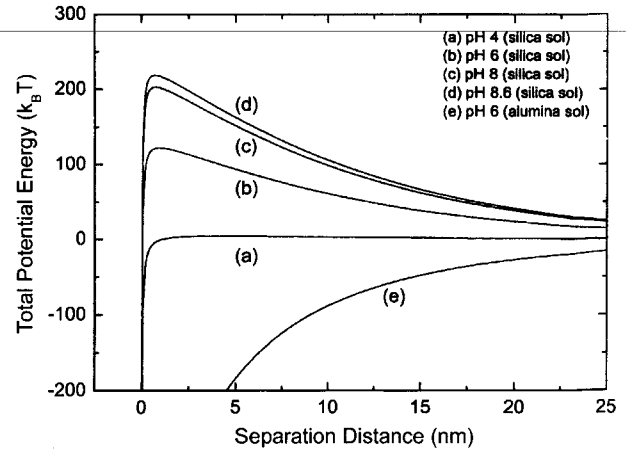


Fig. 6. DLVO plots of total potential energies between silica particle and substrate as a function of separation distance: (a) pH 4 ( $\zeta_1 = \zeta_2 = -10.6$  mV), (b) pH 6 ( $\zeta_1 = \zeta_2 = -43.7$  mV), (c) pH 8 ( $\zeta_1 = \zeta_2 = -55.5$  mV), (d) pH 8.6 ( $\zeta_1 = \zeta_2 = -57.5$  mV) and (e) pH 6 ( $\zeta_1 = -43.7$  mV,  $\zeta_2 = 42.5$  mV).

substrate coated with alumina sol is also shown in Fig. 6. Since there are no data about alumina sol, the zeta potential of alumina at pH 6 ( $\zeta_2 = 42.5$  mV)<sup>5)</sup> and the Hamaker constant ( $A_{12}$ ) for quartz-alumina system ( $1.83 \times 10^{-9}$  J)<sup>14)</sup> were used. Compared with the total potential energy curves for the silica particles in Fig. 3, the total potential energy curves (b), (c) and (d) in Fig. 6 appear to be very similar except the larger potential barrier heights. This results from the fact that the repulsive energy term in equation (6) is two times larger than that in equation (4).

At pH 6, 8 and 8.6, as shown in Fig. 6, there exist large potential barriers ( $>122 k_B T$ ) between the particles and the substrate, which are significantly greater than thermal energy. As a result, the particles in these pH ranges cannot be adsorbed on the substrate. As the repulsive force increases with increasing pH or the zeta potential of the particle, the particle adsorption will be more difficult. However, it can be attributed to adhesion force between the particles and silica sol that, despite the large potential barriers, the particle layers were formed on the substrate.

The surface of the silica particles prepared in this study is predominantly covered with silanols ( $\equiv \text{Si}-\text{OH}$ ) and some water molecules. It has been reported that, for relatively large particles ( $>30$  nm), most silanols are bonded with adjacent silanols by hydrogen bond. Surface of the smaller particles such as silica sol is known to be covered with isolated silanols.<sup>16)</sup> Therefore, the adhesion can arise from a relatively strong hydrogen bond between silanols on the particle surface and silanols in silica sol, or siloxane bonds ( $\equiv \text{Si}-\text{O}-\text{Si} \equiv$ ) formed by condensation reaction at the interface between the silica particles and silica sol.

The arrangement of the particles on the substrate in Figs. 4 and 5 can be related to the state of the particle dispersion in the suspensions. At pH 6, the suspension is less stable than the other suspensions and, therefore, forms the porous

layer with loose packing and irregular arrangement of the particles (Fig. 4(a)). On the other hand, at pH 8.6, the most stable suspension, where the particles are well dispersed, forms the dense layer with uniform packing and regular arrangement of the particles (Fig. 5). Such arrangements are associated with the magnitudes of the repulsive forces existing between the adsorbed particles. Furthermore, the adsorbed particles can maintain their arrangements during drying of the substrate, since the adhesion force due to silica sol may prevent the particles from flocculation by the capillary force that occurs during drying of the substrate.

The particle adsorption from the suspension at pH 4 could not be observed, although relatively weak attractive interactions between the particles and the substrate existed as shown in the DLVO plot in Fig. 6. The particles, which were flocculated at pH 4, could not survive the washing process. It is believed that the adhesion between the particles and silica sol may not be strong enough to hold the flocculated particles.

In contrast to the particle adsorption on the substrate coated with silica sol, the strong adsorption of the particles was observed from the substrate coated with alumina sol. In

the DLVO plot (curve (e) in Fig. 6), the attractive interaction between the particle and the substrate coated with alumina sol is dominant due to the different signs of the zeta potentials of silica particles and alumina sol. As a result, the particles are adsorbed on the substrate by the attractive interactions between the particles and alumina sol. Fig. 7 shows a layer with the particles adsorbed from the suspension at pH 6. The particles were strongly adhered and formed a porous monolayer with a complete coverage of the particles over the entire substrate (Fig. 7(a)). The layer consisted of clusters with less than about 15 particles (Fig. 7(b)). The formation of the monolayer can be explained by that once a single layer of the particles is formed, the excess particles with the same charges of the adsorbed particles are repelled and subsequently washed off. A similar layer has been reported in the adsorption of silica nanoparticles on the surfaces of large alumina particles or alumina fibers.<sup>5)</sup>

#### 4. Conclusion

Spherical particles of colloidal silica (100 nm in size) were electrostatically dispersed and adsorbed on a glass substrate, which had been coated with silica sol or alumina sol. Stability of the suspensions and microstructure of the adsorbed particle layers were discussed in terms of total potential energies between the particles and between the particles and the substrate.

The particle adsorption from the most stable suspension at pH 8.6, where the particles were well dispersed, resulted in a layer with densely packed and regularly arranged particles. The suspension at pH 6, which was less stable than the suspension at pH 8.6, resulted in a porous layer with loosely packed and irregularly arranged particles. However, the adsorption from the suspension at pH 4 could not be observed, although there was a relatively weak attractive interaction between the particles and the substrate. It is believed that the flocculated particles could not adhere on the substrate during the washing step. Despite repulsive interactions between the particles and the substrate coated with silica sol, the adsorption can be attributed to chemical bonds formed at the interface between the particle and silica sol on the substrate.

In contrast, a strong adsorption of the particles at pH 6 was observed on the substrate coated with alumina sol. The particles were strongly adhered due to the attractive interactions between the particles and alumina sol and resulted in a monolayer consisting of clusters densely packed with the particles.

#### REFERENCES

1. P. Sarkar and P. S. Nicholson, "Electrophoretic Deposition (EPD): Mechanisms, Kinetics and Application to Ceramics," *J. Am. Ceram. Soc.*, **79** [8] 1987-2002 (1996).
2. W.-H. Shih, D. Kisailus and W. Y. Shih, "Rheology and

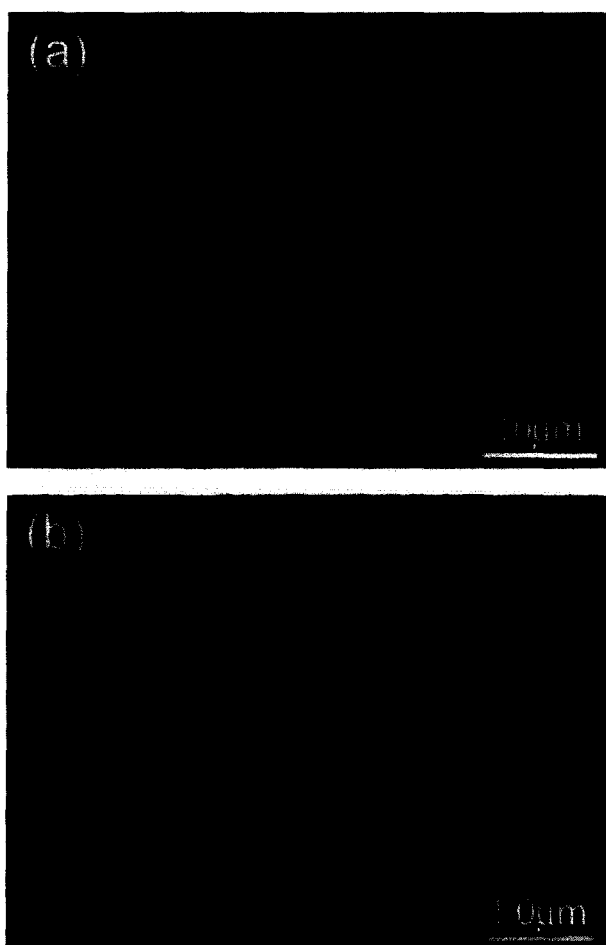


Fig. 7. SEM micrographs of silica particles adsorbed on the substrate coated with alumina sol: suspension at pH 6.

- Consolidation of Colloidal Alumina-coated Silicon Nitride Suspensions," *J. Am. Ceram. Soc.*, **79** [5] 1155-62 (1996).
3. Q. Yang and T. Troczynski, "Dispersion of Alumina and Silicon Carbide Powders in Alumina Sol," *J. Am. Ceram. Soc.*, **82** [7] 1928-30 (1999).
  4. A. Dietrich and A. Neubrand, "Effects of Particle Size and Molecular Weight of Polyethylenimine on Properties of Nanoparticulate Silicon Dispersions," *J. Am. Ceram. Soc.*, **84** [4] 806-12 (2001).
  5. M. L. Fisher, M. Colic, M. P. Rao and F. F. Lange, "Effect of Silica Nanoparticle Size on the Stability of Alumina/Silica Suspensions," *J. Am. Ceram. Soc.*, **84** [4] 713-18 (2001).
  6. J. E. Kolakowski and E. Matijevic, "Particle Adhesion and Removal in Model Systems Part 1.-Monodispersed Chromium Hydroxide on Glass," *J. C. S. Faraday I*, **75** 65-78 (1979).
  7. N. Kallay, "Adhesion of Fine Particles at Solid/Solution Interfaces," *MRS Bull.*, January, 41-7 (1990).
  8. W. Stöber, A. Fink and E. Bohn, "Controlled Growth of Monodisperse Silica Spheres in the Micron Size Range," *J. Colloid Interface Sci.*, **26** 62-9 (1968).
  9. P. C. Hiemenz, *Principles of Colloid and Surface Chemistry*; pp. 690-93, Marcel Dekker, New York, 1986.
  10. A. L. Smith, "Electrical Phenomena Associated with the Solid-liquid Interface," pp. 125-31 in *Dispersions of Powders in Liquids*, Ed. by G. D. Parfitt, Elsevier, New York, 1969.
  11. S. Sadasivan, D. H. Rasmussen, F. Chen and R. K. Kannabiran, "Preparation and Characterization of Ultrafine Silica," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **132** 45-52 (1998).
  12. M. D. Sacks and T.-Y. Tseng, "Preparation of SiO<sub>2</sub> Glass from Model Powder Compacts: I, Formation and Characterization of Powders, Suspensions and Green Compacts," *J. Am. Ceram. Soc.*, **67** [8] 526-31 (1984).
  13. B. V. Derjaguin, *Theory of Stability of Colloids and Thin Films*, Consultant Bureau, New York, 1989.
  14. L. Bergström, "Hamaker Constants of Inorganic Materials," *Advances in Colloid and Interface Science*, **70** 125-69 (1997).
  15. R. Hogg, T. W. Healy and D. W. Fuerstenau, "Mutual Coagulation of Colloidal Dispersions," *Trans. Faraday Soc.*, **62** 1638-51 (1965).
  16. H. Kamiya, M. Mitsui, H. Takano and S. Miyazawa, "Influence of Particle Diameter on Surface Silanol Structure, Hydration Forces and Aggregation Behavior of Alkoxide-Derived Silica Particles," *J. Am. Ceram. Soc.*, **83** [2] 287-93 (2000).