Formation of Ordered Monolayer of Anionic Silica Particles on a Cationic Molecular Layer

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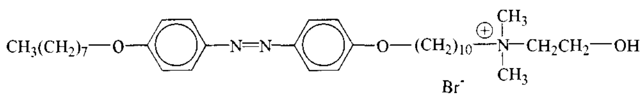
Quartz crystal microbalance (QCM) measurements and scanning electron microscopy revealed the formation of defect-free monolayer of anionic silica nanoparticles on a solid substrate coated with a cationic organized molecular layer.

Nanoparticle research has witnessed tremendous growth from expectation to obtain unique functional materials.[1] Especially, designed architecture of nanoparticles is of great importance for realization of nano-sized devices for which methodologies to prepare two- and three-dimensional regular arrays of inorganic nanoparticles is indispensable.[2]

Preparation of densely-packed monolayers of inorganic nanoparticles is not easy. Careful drying or dip-coating of organosols of nanoparticles gives their two-dimensional arrays on solid substrates,[3] but particle disposition within the array is usually not regular. Polyelectrolytes and self-assembled monolayers (SAM) are often used as underlying substrates for organization of inorganic particles.[4] However, irregularly-located charges of polyelectrolytes on a substrate are not suitable for obtaining densely- and regularly-packed monolayers of charged particles. Densely-packed layers of silica particles were produced by alternate assembly with linear polycations when sodium chloride was added in order to reduce electrostatic repulsion among adsorbing particles,[6] but the addition of salts led to *multi*layer stacking. This is not useful for formation of regularly-packed *mono*layer of nanoparticles. Thick films of densely packed silica particles can be obtained by electrophoretic deposition,[7] but monolayer formation has been reported in the case of metal nanoparticles.[8]



$CH_3(CH_2)_7-O-C_6H_4-N=N-C_6H_4-O-(CH_2)_{10}-\overset{\oplus}{N}(CH_3)_2-CH_2CH_2-OH \; Br^-$

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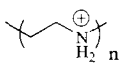
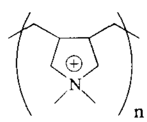
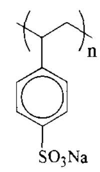


PEI



PDDA



PSS

A substrate with a high charge density is probably required in order to prepare a monolayer of densely-packed charged particles. Ionic bilayer membranes possess regularly- and densely-packed arrays of charged head groups on the membrane surface.[9] They can provide regular multilayers by alternate adsorption with linear polycations. For instance, $C_8AzoC_{10}N^+C_2OH$ (**1**), that forms an interdigitated bilayer structure[10] and sodium poly(4-styrenesulfonate) (PSS), gave alternate multilayers in which the mole ratio of **1**/PSS was 1.5 : 1.[11]

We have tried to obtain a closely-packed monolayer of citrate-stabilized gold nanoparticles on amphiphile **1**,[12] but defects are always found in the particle layer probably due to polydispersity of the particles. Based on these experience, we assumed that the combination of highly charged surfaces and monodisperse particles are indispensable for formation of defect-free monolayers of charged particles.

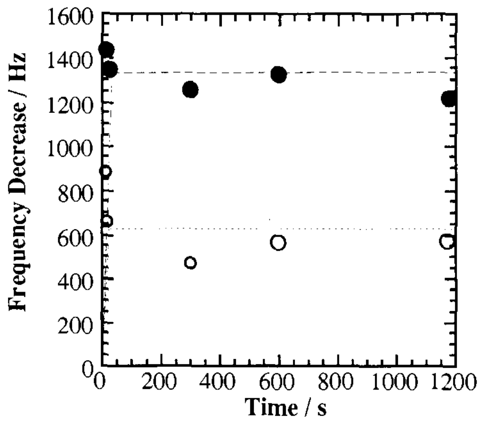


Figure 1. Time course of frequency decrease due to adsorption of SiO_2 nanoparticles onto PDDA (○) and amphiphile **1** (●). 20 °C; particle diameter = 25 nm; particle concentration = 100 mg cm^{-3}; pH = 10.

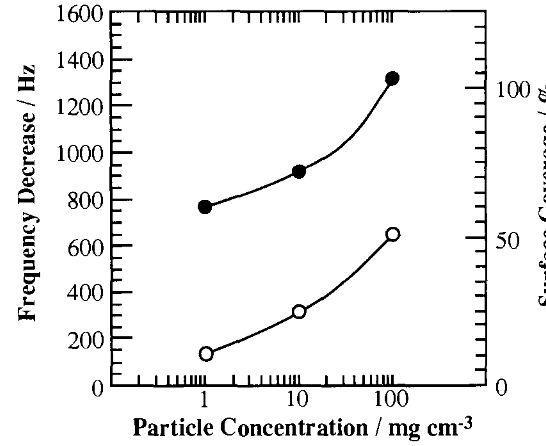


Figure 2. Effects of the SiO_2 concentration on its adsorption on PDDA (○) and amphiphile **1** (●). 20 °C; particle diameter = 25 nm; adsorption time = 20 min; pH = 10.

An aqueous dispersion of silica nanoparticles used here was provided by Nissan Kagaku ("Snowtex"). The average diameter of the spherical particle was 25 ± 5 nm. Amphiphile **1** was prepared as reported.[10] Poly(ethyleneimine) (PEI, Wako, MW = 60 000), poly(diallyldimethylammonium chloride) (PDDA, Aldrich, medium MW), and PSS (American Polymer Standards, MW = 88 000) were used as received. Silver-coated QCM (9 MHz, AT-cut) resonators were immersed for given periods of time in aqueous solutions of either polyelectrolytes or bilayer **1** (20 min), and silica particles (5 sec ~ 20 min), dried under

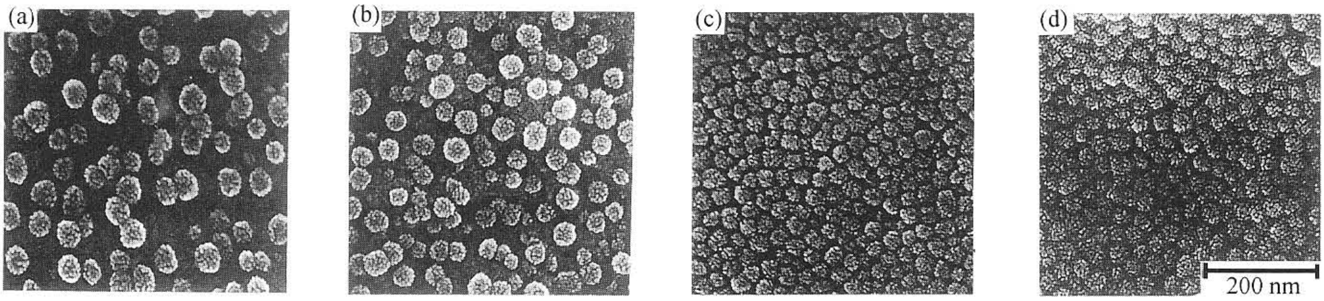


Figure 3. SEM images of SiO_2 nanoparticles adsorbed on PDDA (a, b) and amphiphile **1** (c, d). Adsorption time was 5 sec (a, c) and 20 min (b, d). 20 °C; particle diameter = 25 nm; concentration = 100 mg cm^{-3}; pH = 10; acceleration voltage = 25 kV; Pt coating 2 nm.

nitrogen, followed by frequency measurements. All experiments were conducted at 20 °C.

A well-defined precursor film of PSS and PEI was assembled onto resonators with a thickness of *ca.* 10 nm. The precursor film contained eight polyion layers beginning with PEI in the alternate mode PEI/PSS and the terminal layer was *negative* PSS. The resonator was then immersed for 20 min in an aqueous solution of PDDA or **1**, washed with water, and immersed in a dispersion of silica nanoparticles. The adsorption of **1** on the precursor layer gave a frequency decrease (ΔF) of 170 Hz on average, indicating formation of interdigitated bilayer.[10, 11] Adsorption of PDDA gave a ΔF of 130 Hz on average.

Figure 1 shows the time course of adsorption of silica particles (100 mg/cm^3) onto the precursor layers of **1** and PDDA, as measured by QCM. Surprisingly, the adsorption was saturated in both cases as early as 5 sec after the immersion of the substrates. The adsorbed mass was much greater on the amphiphile layer **1** than that on the layer of PDDA.

The magnitude of the frequency decrease is enhanced with increasing silica concentrations (Figure 2). The coverage of the QCM resonator by silica particles is also indicated in this figure. If the ideal hexagonal packing is attained for a monolayer of silica particles with a diameter of 25 nm, a flat QCM resonator will give a frequency decrease (ΔF) of 1270 Hz[13] (100% coverage). The calculated coverage was 106 % at the particle concentration of 100 mg/cm^3 on the layer **1**.

In Figure 3, typical SEM photographs of layers of the adsorbed silica particle are collected. SEM images are essentially identical at immersion times of 5 sec and 20 min as expected from the saturation phenomena of Figure 1. On the PDDA-coated surface (Figure 3(a, b)), most particles are scattered independently without forming closely packed structures. Similar situations have been reported for charged inorganic nanoparticles adsorbed onto oppositely-charged surfaces of polyions[4a, 4b] or a coordinative surface of SAM.[4c-4f] In contrast, uniformly- and densely-packed layers of silica particles are created over a large area on the surface of amphiphile **1** (Figure 3(c, d)). To our knowledge, the formation of the defect-free monolayer of ionic particles by simple immersion has not been reported. These images were found in the whole area of the resonator.

On PDDA surface, the surface charge is reversed upon excessive adsorption.[6b] Therefore, negatively-charged silica particles are repelled with each other without addition of salts. In contrast, the more highly charged surface of layer **1** may supress such electrostatic repulsion of silica nanoparticles to form closely-packed structures. Furthermore, the flatness of the surface of amphiphile layer appears convenient for the adsorbed particles to form an ordered structure. At the same time, high monodispersity of the particles is an important factor for the preparation of ordered layers. Spherical particle cannot be packed regularly without unique size.

In conclusion, a close-packed defect-free monolayer of monodisperse anionic silica nanoparticles was successfully prepared by adsorption onto a highly-charged layer of a cationic amphiphile. This procedure is facile, inexpensive and can be applied to the preparation of ordered monolayer of other functional charged nanoparticles.

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13 The relationship between adsorbed mass M (g) and frequency decrease ΔF (Hz) in this system is $\Delta F = 1.83 \times 10^8 \times M/A$,[14] where A is the apparent area of the QCM. By using the coefficient of the two dimensional packing, 0.9069, and the density of silica (ρ), 2.3 g/cm^3, the number of particles adsorbed on both sides of the resonator is $N_a = (0.9069 \times 2A)/\pi r^2$, where r is the average radius of the silica particles (12.5 nm). The adsorbed mass is $M = \rho \times 4/3(\pi r^3) \times N_a$.

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