Alternately Assembled Ultrathin Film of Silica Nanoparticles and Linear Polycations

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(Received October 23, 1996)

Anionic silica nanoparticles were assembled with linear polycation by alternate adsorption technique. Regular growth and surface smoothness of the films were confirmed by QCM and SEM, respectively.

The preparation of organic/inorganic nano-sized hybrids is one of the most important targets in current materials chemistry. Inorganic nano-structures may be prepared at the surface of Langmuir-Blodgett films or in interlayers of cast bilayer films.[1–5] Alternate layer-by-layer assembly[6] that is based on neutralization and resaturation of surface charge is a novel promising approach, because film thickness and layer order can be readily controlled (Figure 1). Our previous results on the

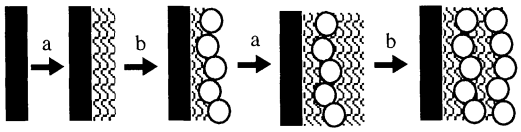
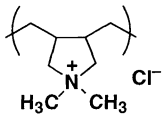


Figure 1. Schematic illustration of alternate assembly of colloidal silica and PDDA: a, silica adsorption; b, PDDA adsorption.

assembly of inorganic microplates (clay) and globular proteins clearly demonstrated that this approach is not limited to linear polyions.[7] In fact, Iler's pioneering work was concerned with alternate assembly of colloidal particles.[8] Fendler *et al.* also reported polyion/semiconductor composite films.[9] We describe in this article that silica nano-particles can be assembled alternately with linear polycations.



PDDA

Three kinds of colloidal silica (Nissan Kagaku, Japan), which have diameters of 25-nm, 45-nm, and 78-nm and negatively charged at pH 10, were assembled with poly(diallyldimethyl-ammonium chloride) (PDDA) on a quartz crystal microbalance (QCM, AT-cut, 9 MHz, Ag-electrode) by alternately dipping the QCM plate in aqueous solutions of colloidal silica and polyion, as described previously ([Silica] = 10 mg/mL, [PDDA] = 3.0 mg/mL, and immersion time = 20 min).[10] The frequency decreases (mass increases) observed at each step are shown in Figure 2. Regular film growth was found in all cases. The average $-\Delta F$ value of silica adsorption step is 520 Hz for 25-nm particles, 900 Hz for 45-nm particles, and 1350 Hz for 78-nm particles, and correspond to ca. 70% of hexagonally packed layers of silica particles.[11] In the *in situ* QCM measurement,[12] the adsorption was shown to reach saturation only 10 sec after film immersion. Therefore, silica adsorption is spontaneously terminated, giving a highly reproducible film-growth step.

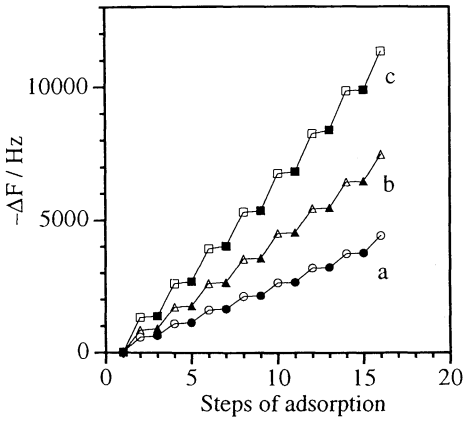


Figure 2. Frequency decrease of QCM upon film assembly (open plot, PDDA adsorption; filled plot, silica adsorption): a, 25-nm silica; b, 45-nm silica; c, 78-nm silica ([Silica] = 10 mg/mL and [PDDA] = 3.0 mg/mL).

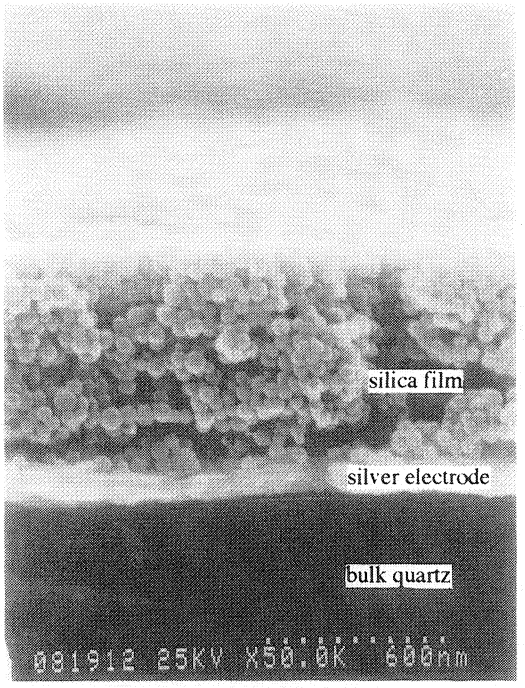


Figure 3. Cross-sectional SEM image of $\{(PDDA/PSS)_2 + PDDA + (SiO_2/PDDA)_8\}$ film assembled on a silver QCM electrode in the presence of 0.1 M NaCl (45-nm silica was used).

Growth of the silica layer depends on concentrations of silica and co-existing inorganic salt. Assembly of 45-nm silica and PDDA gave frequency decreases of 80, 570, 900, 1350, and

1700 Hz at 0.1, 1, 10, 100, and 231 mg/mL of silica, respectively. Frequency decreases for 45-nm particle (10 mg/mL) with 0, 0.01, 0.1, and 0.25 M NaCl are 900, 1400, 4300, and 6500 Hz, respectively. In spite of these large mass variations, the adsorption reached saturation quickly, and stable film growth was obtained in all cases. An increase in ionic strength of the silica solution would decrease effective charge and permit thicker layers to be formed. Interestingly, the most smooth surface was obtained in the film assembled with 0.1 M NaCl. An SEM image of the film (Figure 3) shows a rather flat surface in spite of large sizes of the individual particles. Experimental conditions that affect film morphology are under investigation.

Similarly successful multilayer assembly was achieved for other charged nano-particles: cationic cerium oxide (pH 3.5) with poly(sodium styrenesulfonate) (PSS), anionic titanium oxide (pH 10) with PDDA. This technique would be widely applied to assembly of inorganic-organic nano-structured materials, leading to development of a new class of ceramic and semiconductor devices.

References and Notes

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11 Comparison between SEM and QCM data reveals the relation between thickness (d) and frequency decrease ($-\Delta F$) as follows: d (nm) = $-0.022\ \Delta F$ (Hz). Two-dimensional hexagonal packing of spheres has the same mass as that of a uniform film with thickness of 60.5% of the sphere's diameter.
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