Fabrication of Self-assembled Polymer Particle Monolayers on Gold Substrates

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(Received August 9, 2002; CL-020676)

Polymer particles bearing sulfonium groups are found to be self-assembled on a gold substrate by simply immersion into latex. Millimeter-sized large domain of 2-D highly ordered particle arrays were also obtained in a self-assembled particle monolayer. Polymer particles were selectively assembled on a patterned gold substrate at the particle size level by a combination with photolithographic technique.

Self-assembled monolayers (SAMs) are the most widely studied and best characterized examples of surface modification of solid surfaces.[1] The well-known systems of SAMs are usually prepared by dipping a gold substrate into the organic solution of alkanethiolates $CH_3(CH_2)_nS^-$.[2–4] In these decades, a number of attempts have been devoted to construct the highly ordered particle assemblies, because textured surfaces with strictly controlled periodicity and morphology have been expected as the potential use in many industrial areas, such as gratings, interferometers, and antireflection coatings. Conventional methods for organizing the spherical colloids on a sold support were based on electrostatic attractive interactions between particles and substrates, the capillary forces in the liquid layer, electrohydrodynamic mechanism, etc.[5–9] Although hexagonally closed-packed microcrystalline structures of particle monolayer were satisfactory obtained by means of above technique, these methodologies required specialized apparatus and highly advanced skills for the controlled assembling of colloidal particles. We've reported preparation and utilization of reactive polymer latex particles P(ST-*co*-MAPDS) (Figure 1) synthesized by emulsifier-free emulsion copolymerization of styrene (ST) with methacryloyloxyphenyldimethylsulfonium methylsulfate (MAPDS) using 2,2′-azobis(2-amidinopropane) dihydrochloride (V-50) as an initiator.[10–12] Recently, it has been found that P(ST-*co*-MAPDS) particles have excellent self-assembling properties to organize a particle monolayer on a gold substrate. In the present study, we reports on fabrication of self-assembled polymer particle monolayers on gold substrates and the possibility to construct 2-D highly ordered particle arrays.

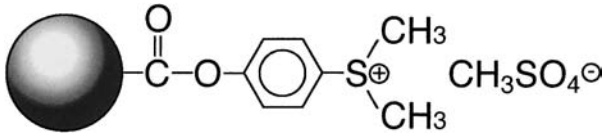

Figure 1. P(ST-*co*-MAPDS) particles.

Preparation of P(ST-*co*-MAPDS) latex particles was described elsewhere.[10] P(ST-*co*-MAPDS) latex was purified by a repetitive centrifugation and redispersion process in deionized water several times in order to remove water soluble polymer and electrolytes. Number-averaged diameter (d_n) and the standard deviation (σ) of P(ST-*co*-MAPDS) particles were determined to be 226 nm and 3.01 by SEM (JOEL, JSM-5310) observation, respectively. A gold substrate prepared by sputtering deposition of Au on a silicon wafer ($10 \times 30 \times 0.6$ mm), was immersed into 0.1 wt% of P(ST-*co*-MAPDS) latex at 20 °C and sequentially washed with distilled water and methanol to remove weakly adsorbed particles. Selective assembling of P(ST-*co*-MAPDS) particles on a gold substrate was carried out by a combination with photolithographic technique. The spin-coated photoresist film (Nippon Zeon, ZPP1700PG) on a gold substrate was irradiated through a mask using a mercury lamp. After the development of irradiated photoresist film, the obtained patterned gold substrate was immersed into P(ST-*co*-MAPDS) latex for 2 h. Surface morphology of polymer particle monolayers on a gold substrate was observed with SEM.

Figure 2 shows the SEM image of P(ST-*co*-MAPDS) particles spontaneously adsorbed on a gold substrate. P(ST-*co*-MAPDS) particles were homogeneously self-assembled on a gold substrate at regular intervals between each particle. On the contrary, P(ST-*co*-MAPDS) particles rarely adsorbed on a gold substrate hydrophobically modified with dodecanethiol, which indicates that hydrophobic interaction between a polymer particle and a gold substrate is not a dominat factor for self-assembling of polymer particle in this system. The formation mechanism of the self-asembled P(ST-*co*-MAPDS) particle monolayer may be attributed to self-assembling interaction between a sulfonium group and a gold substrate as reported in the alkanthiol/gold system.

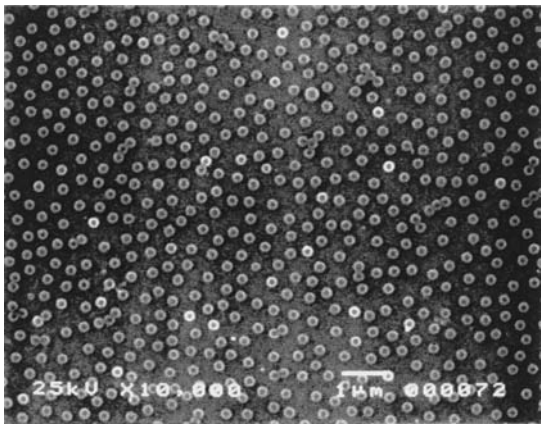

Figure 2. SEM image of self-assembled P(ST-*co*-MAPDS) particle monolayer on a gold substrate.

It could be easily recognized that ~20% of a gold substrate is covered with a lot of brilliant domains that have areas of $5 \times 5\,mm^2$ at the maximum size. The SEM image shows that these domains are consisted of the tetragonally packed P(ST-*co*-MAPDS) particle arrays with a regular interval (Figure 3). This unique morphology of self-assembled P(ST-*co*-MAPDS) particle

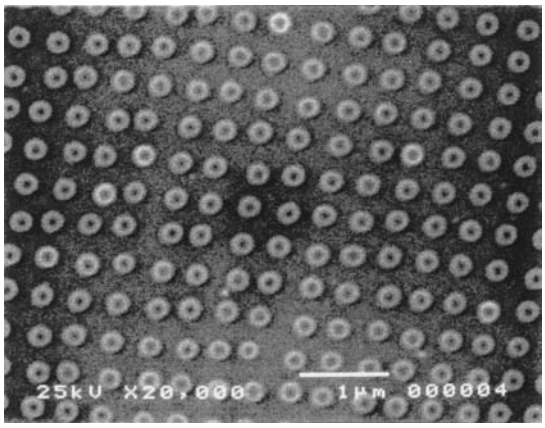

Figure 3. Tetragonally packed self-assembled P(ST-*co*-MAPDS) particle arrays with a regular interval on a gold substrate.

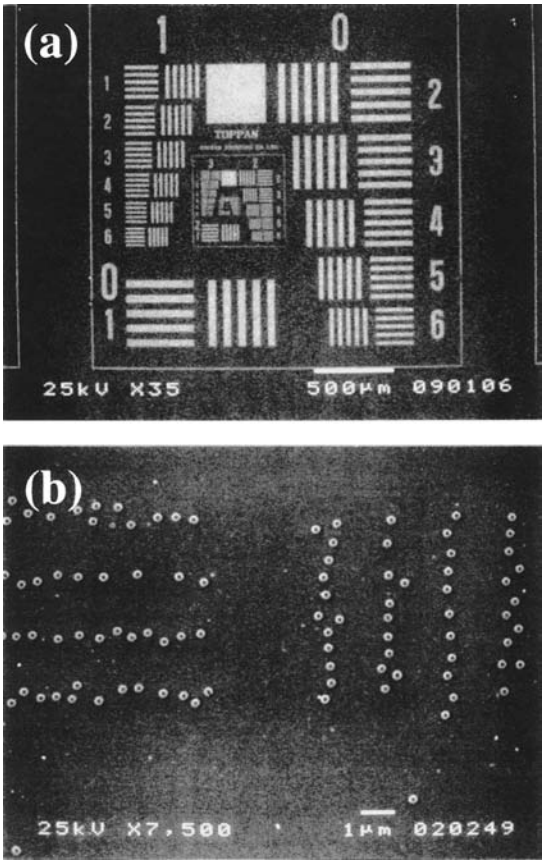

Figure 4. SEM images of selective deposition of P(ST-*co*-MAPDS) particles on a patterned gold substrate. (a) Fine patterns drawn with deposited P(ST-*co*-MAPDS) particles on a gold substrate (white parts). (b) P(ST-*co*-MAPDS) particles selectively deposited at the particle size level.

monolayer may be due to the balance of self-assembling interaction of sulfonium groups and repulsive electrostatic forces between particles. It was also found that particle aggregates slightly synthesized as by-products ($\ll$1%) intensely transform the ordered structure into the randomly deposited configuration, which implys that highly monodispersed latex particles are crucial for the formation of large-sized 2-D ordered particle domains. As the detailed mechanism and kinetics of spontaneous ordering is still uncertain, the further investigation is now in progress to obtaine the highly structured large particle assemblies by using extremely monodispersed P(ST-*co*-MAPDS) latex particles.

Figure 4 demonstrates the microscopic photograph of selective deposition of P(ST-*co*-MAPDS) particles on a patterned gold substrate. Evidently, the SEM image indicates that patterns can be drawn with a deposited P(ST-*co*-MAPDS) particles (Figure 4a). Figure 4b displays that P(ST-*co*-MAPDS) particles were successfully deposited at a resolution of 0.8 μm line-and-space, which is the highest resolution of the photomask employed in this study.

This work was partially supported by a Grant-in Aid for Encouragement of Young Scientists from the Ministry of Education, Culture, Sports, Science and Technology, Japan (No. 13750810). We would like to thank Koji Inogai and Yukiko Kanamori at SCG Japan Ltd. for providing silicon wafers. We would also like to thank Dr. Junji Kido for his help with spin coating technique.

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