Patterning of Gold Surfaces with Hexadecanethiol by Shear Force-based Scanning Capillary Microscopy

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A shear force-based scanning capillary microscope was fabricated by contacting a glass capillary with a quartz crystal tuning fork and was used for the patterning of gold surfaces with hexadecanethiol. A micrometer-sized pattern was successfully obtained by moving the capillary, through which the hexadecanethiol solution was introduced, along the gold surface. Dotted and line patterns were observed by high-resolution scanning electrochemical microscopy using a standing approach mode in (ferrocenylmethyl)trimethylammonium (FA^+) solution without destroying the morphology of the surface.

Scanning probe microscopy techniques, such as scanning atomic force microscopy (AFM)[1] and scanning electrochemical microscopy (SECM)[2–6] are widely used for the micro/nanoscale patterning of surfaces. In particular, micropatterning using a micro/nano pipette or capillary[7–9] through which various molecules can be introduced has a wide range of applications and the potential to improve the resolution of the pattern. Patterning of a resist on gold-sputtered glass,[7] copper deposition on gold and silicon,[8] and silver deposition on gold[9] have been reported. Patterning has been performed by moving the capillary tip along the surface, regulating the distance between the tip and the surface. Shear force control has been employed to regulate the distance using a tuning folk,[10–13] and Fresnel diffraction by focusing a laser beam on the tip.[14,15]

Dip-pen nanolithography[16] is widely used for nanoscale patterning of alkanethiol, but unsuitable for fabricating micropattern of biomolecules directly. Using micropipette, various solutions can be introduced in the micropipette. Therefore, direct fabricating the pattern of various molecules can be possible. In this report, a shear force-based scanning capillary microscopy has been applied to the micropatterning of gold surfaces with hexadecanethiol using a micropipette.

(Ferrocenylmethyl)trimethylammonium (FA^+) perchlorate was synthesized according to the literature.[13] All the aqueous solutions were prepared with water purified using a Milli-Q Jr (Millipore Co.). Hexadecanethiol (Wako Chemical) was used as received.

A section of lead glass (World Precision Instruments, PG10150-4) was pulled with a capillary puller and a gold wire (diameter 100-μm) was inserted into the capillary. The tip was fused using a microforge (Narishige, Tokyo model MF-900). The tip was polished first on a turntable (Narishige, Tokyo model EG-4), and finally with a fine emery paper (Sumitomo 3M, Tokyo #15000), to obtain a disk-shaped Au electrode. The disk-shaped Au electrodes were cleaned thoroughly by washing them with distilled water and ethanol for 10 min in a supersonic bath and were used as substrate for patterning.

A glass tube (1.5-mm diameter, Terumo, Japan) was pulled with a capillary puller (Narishige, Tokyo model PC-10) so as to form a 1–2-μm capillary tip. A quartz crystal tuning fork (Citizen, CFS-308) was soldered onto a diaphragm of commercially available piezoelectric transducer in order to excite the mechanical resonance of the tuning fork, and the pulled capillary was contacted with one prong of the tuning fork (Figure 1), forming a shear force-based probe. Since the tip of the capillary vibrates with the prong of the tuning fork without glue, the capillary is not glued to the tuning fork to use the tuning fork repeatedly. A 20-μL portion of a 20 mM hexadecanethiol/(70% ethanol, 30% glycerol) solution was introduced into the pulled capillary, and it was installed in the shear force-based probe described above. To draw a dotted pattern, the tip of the capillary was brought near the gold surface (in air) at a rate of 0.1–0.5 μm/s until the amplitude of the tuning fork was damped to 50% of the starting amplitude, and then movement of the probe was stopped and it was held in place for 1–5 s. The tip was then retracted and moved laterally to the next point. By repeating this procedure, an array of dots was obtained. When the space between the dots was less than 1 μm, a line pattern was obtained. After drawing the pattern, the Au electrode was washed with ethanol and distilled water. The movement of the capillary was performed with the SECM system described previously.[12]

A 0.4-μm radius Pt disk microelectrode was used for SECM probe. An SECM system and fabrication of the SECM probe were described previously.[12] The standing approach mode[12] was used to image the electrochemical activity of the surface.

To check the performance of the capillary probe, a Pt band array electrode (Pt layer 0.15-μm thick) was imaged using the standing approach mode in air. The width of the Pt and space was 10 μm. A 60 × 60-μm^2 topographic image of the Pt array electrode obtained with an empty capillary probe is given in Figure S1.[17]

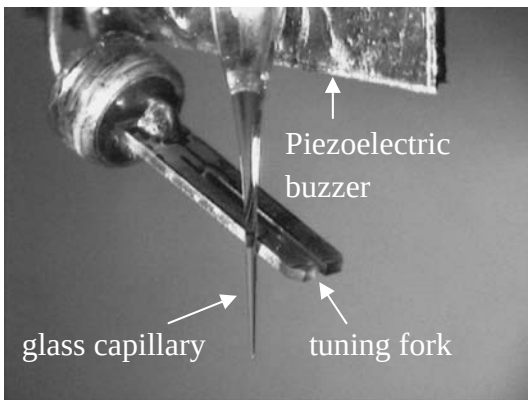

Figure 1. Photograph of a shear force-based capillary probe.

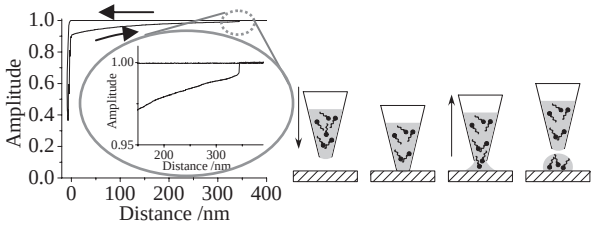

Figure 2. Change in amplitude of the tuning fork during extension and retraction of a capillary tip filled with 20 mM hexadecanethiol/(70% ethanol, 30% glycerol) solution.

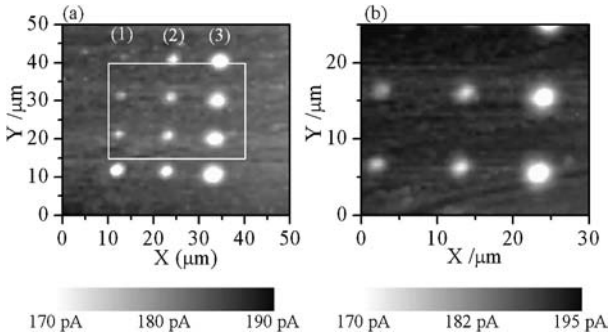

Figure 3. SCEM images, (a) $50 \times 50\,\mu m^2$ and (b) $30 \times 25\,\mu m^2$ in size, of the hexadecanethiol-patterned Au surface obtained using a 0.4-μm Pt microelectrode in 1.0 mM FA^+ solution. In (a), (1) indicates 1-s capillary hold time, (2) 2 s, and (3) 5 s.

To draw a dot pattern of hexadecanethiol on the Au surface, the shear force-based capillary probe was moved toward the surface until the amplitude of the tuning fork decreased to 50% of the starting amplitude, and after standing for several seconds, the tip was retracted. Figure 2 shows the change of amplitude of the tuning fork when the tip of the capillary was brought near to the Au surface and retracted at a rate of 0.1 μm/s. When the tip was touched to the surface, the amplitude of the tuning fork suddenly decreased. During retraction, a sudden recovery of the amplitude (up to 90% of starting amplitude) was observed. At this point, the tip and the Au surface disintegrated, but a small portion of the solution remained between the tip of the capillary and the surface. When the tip was moved away, the amplitude gradually increased and recovered to 100% of the starting amplitude at 350 nm, where the solution remaining on the Au surface disintegrated with the tip of the capillary.

Figure 3a shows an SECM image of the dot pattern on a Au surface obtained with a 0.4-μm Pt microelectrode in standing approach mode in 1.0 mM FA^+ solution. When the tip of the capillary contacted the surface, the movement of the tip was stopped for (1) 1 s, (2) 2 s, and (3) 5 s to allow the solution of hexadecanethiol to spread on the gold surface. Four dots were placed on the surface for each of the three holding times. The size of the dots increased with increasing holding time. The area enclosed by the solid line was imaged with higher resolution (Figure 3b). A 4×4 dotted pattern (Figure 4a) and line pattern (Figure 4b) were also obtained by moving the tip of the capillary in a programmed pattern. Line pattern was obtained by drawing the dots at intervals of 0.5 μm. To draw a clear pattern, the viscosity of the solution in the capillary is important. When 85% ethanol/15% glycerol was used as the solvent, the pattern spread to ca. 10-μm wide using a 1-μm capillary.

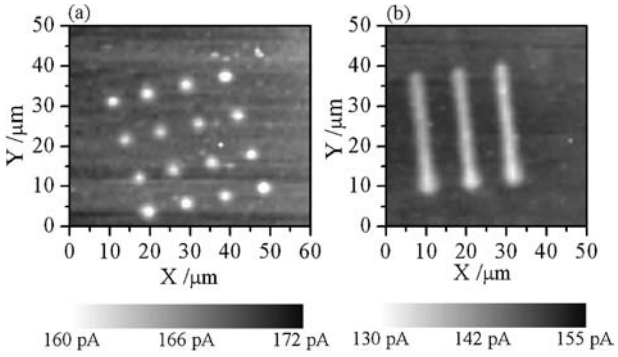

Figure 4. SCEM images of 4×4-dotted pattern (a) and line pattern (b) on Au surface with hexadecanethiol, obtained with 0.4-μm Pt microelectrode in 1.0 mM FA^+ solution.

Micropatterning of a surface with hexadecanethiol using shear force-based scanning capillary microscopy has been demonstrated. Instead of hexadecanethiol solution, various molecules can be introduced in the micropipette. This method may be applied for the patterning of biomolecules such as enzymes, antibodies or DNA.

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17 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

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