Patterning a Preformed, Reactive SAM Using Microcontact Printing

Lin Yan, Xiao-Mei Zhao, and George M. Whitesides*

Department of Chemistry and Chemical Biology
Harvard University, 12 Oxford Street
Cambridge, Massachusetts 02138

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This paper describes a convenient methodology for the generation of patterned structures on the surface of a self-assembled monolayer (SAM) of alkanethiolates on Au and Ag that combines microcontact printing (μCP)[1] and chemical reaction.[2] A number of reports have described syntheses of patterned structures on preformed SAMs using chemical methods: These methods have typically used either a photochemical pattern transfer step to produce micrometer-scale patterns[3−5] or atomic force microscopy (AFM) to generate patterns at the nanometer scale.[6,7] These methods require alkanethiols that can be inconvenient to synthesize and are often not compatible with complex or sensitive organic groups. In addition, photochemical methods and AFM methods are difficult to use over large areas and on curved substrates.

Microcontact printing (μCP) of alkanethiolates on Au and Ag is a general technique for patterning SAMs over large areas and on curved surfaces.[1] This method is compatible with a wide range of organic functionalities but does require separate synthesis of each thiol that is to be patterned. Here, we demonstrate a new method to pattern SAMs that extends and simplifies conventional μCP and several applications of this method, including the synthesis of a patterned SAM on Au with regions presenting thiol groups: This type of patterned surface cannot be readily obtained using conventional μCP. We have used this surface to pattern the deposition of Au nanoparticles.

Figure 1 depicts this method. A reactive SAM presenting interchain carboxylic anhydrides was prepared using the procedure described previously.[2] A poly(dimethylsiloxane) (PDMS) stamp with protruding features (squares ~10 μm on a side) on its surface was inked with *n*-hexadecylamine and placed in contact with the substrate for 1 min. The anhydride groups in the regions that contacted the stamp reacted with amines and produced a mixed SAM comprising a ~1:1 mixture of *N*-alkyl amides and carboxylic acids.[8] The remaining anhydride groups in the uncontacted regions were allowed to react with another amine, $CF_3(CF_2)_6CH_2NH_2$, to give a patterned SAM having regions presenting *N*-hexadecyl amides and fluorinated *N*-alkyl amides.[9] All of these reactions were carried out under ambient experimental conditions, and the complete procedure—from a SAM presenting carboxylic acids to a patterned SAM—required less than 1 h.

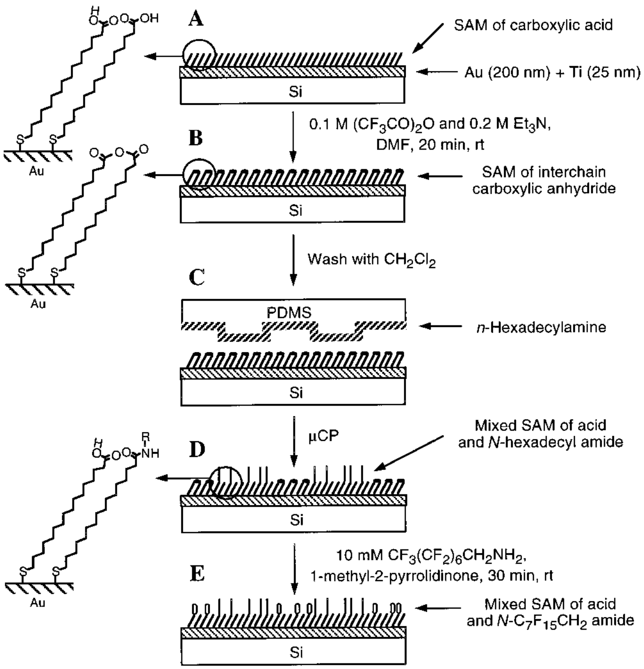

Figure 1. Schematic representation of the procedure for patterning a SAM that presents two different *N*-alkyl amides using μCP and chemical reaction. The diagram represents the composition of the SAM, but not the conformation of the groups in it.

Scanning electron microscopy (SEM) and secondary ion mass spectroscopy (SIMS) defined both the edge resolution and composition of such patterned SAM (Figure 2). SEM images indicate that the edge resolution of these squares was at submicrometer scale ($\leq$100 nm)[10] and, although somewhat larger than that obtained for μCP of alkanethiolates on Au (~50 nm),[11] entirely adequate for many applications in microfabrication, and especially in biochemistry and cell biology.[12] The high contrast and uniformity in the SEM and SIMS images (particularly in Figure 2D) suggest that μCP delivered a well-defined pattern of *n*-hexadecylamine to the reactive SAM on both Au and Ag.

We estimated the yield of the chemical reaction on Au carried out by μCP relative to that by immersion using two procedures: First, we compared the ellipsometric thickness increase (Δh) of the mixed SAM prepared by μCP using a flat PDMS stamp to that by immersion, assuming that the reaction yield was proportional to Δh. We found that Δh of these mixed SAMs followed the empirical relationship between Δh of the mixed SAM and the length of alkylamine that we derived previously.[2] Table 1 shows that Δh of these two SAMs were the same, as were the contact angles of distilled, deionized water.[13] This result suggests that the mixed SAMs prepared by μCP and by immersion were structurally similar. Second, we allowed these mixed SAMs to react further with $CF_3(CF_2)_6CH_2NH_2$, assuming that the unreacted anhydrides in the regions contacted by the stamp would react with this amine to incorporate fluorine into the SAM. XPS study showed that such treatment introduced a weak F(1s) signal in

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[8] The reaction between alkylamines and interchain carboxylic anhydrides generated a SAM presenting a mixture of *N*-alkyl amides and carboxylic acids, and there were no detectable amounts of alkylamines physisorbed electrostatically to the carboxylates (see ref 2). We have *directly* printed *n*-hexadecylamine on the SAM of carboxylic acid and found that the resulting patterns on the SAM of the acid were readily washed away using either acidic (pH = 1) and basic (pH = 13) buffers; whereas, the patterns on the reactive SAM did not change under these conditions.

[9] The advancing contact angle of water on the $CF_3(CF_2)_6CH_2NH_2$-modified SAM was 100°, and the receding contact angle was 88°. The contact angles on a homogeneous SAM of $CF_3CH_2NHCOCH_2SH$ were $\theta_a = 99°$ and $\theta_r = 75°$ (Tam-Chang, S.-W., et al. *Langmuir* **1995**, *11*, 4371−4382); the contact angle on a homogeneous SAM of $CF_3(CF_2)_9SH$ was $\theta_a = 118°$ (Chidsey, C. E. D., et al. *Langmuir* **1990**, *6*, 682−691).

[10] The edge resolution of the pattern was perhaps limited by the morphology of the polycrystalline gold substrate and the edge roughness of the PDMS stamp.

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[13] The values of contact angles for the mixed SAMs are independent of the pH values of the aqueous buffers used for measurement over the range of pH = 1−13.

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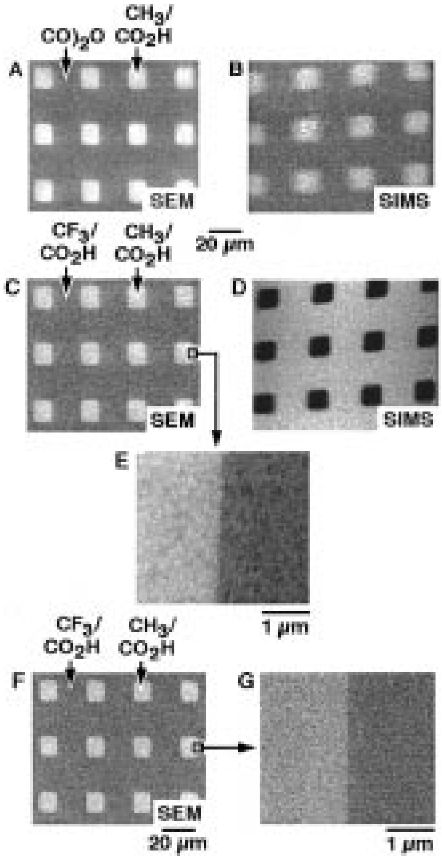

Figure 2. Characterization using SEM and SIMS of the patterned SAMs on Au (A−E) and on Ag (F and G) generated by μCP of *n*-hexadecylamine on the reactive SAM followed by reaction with $CF_3(CF_2)_6CH_2NH_2$. The light areas in the SEM images were the regions that contacted the stamp. The light squares in SIMS image B contained nitrogen while the dark regions did not; the light regions in SIMS image D had fluorine while the dark squares did not. The patterns in the SIMS images were distorted because the sample holder was slightly tilted during acquisition of these images.

Table 1. Comparison between Mixed SAMs Prepared by μCP and Immersion[a]

	contact angle (deg)		thickness increase
mixed SAMs	θ_a	θ_r	(Δh) (Å)
by μCP	100	85	12.2 ± 1.6
by immersion	101	86	12.3 ± 2.4

[a] For μCP, a flat PDMS stamp was inked with a 5 mM 2-propanolic solution of *n*-hexadecylamine and placed in contact with the reactive SAM for 1 min after evaporation of the solvent. For immersion, a substrate of the reactive SAM was dipped in a 10 mM solution of *n*-hexadecylamine in 1-methyl-2-pyrrolidinone for 30 min. Both samples were washed with ethanol and dried in a stream of nitrogen before the measurements were taken. The thickness increase was the difference between the ellipsometric thickness of the mixed SAM and that of the SAM of the acid, and the values were the averages over measurements of three samples; the values of contact angle of water were the averages of measurements of three samples.

both SAMs; the intensities of the F(1s) signals correspond to 5% of that of the SAM prepared by reaction of the reactive SAM directly with the fluorinated amine. The weak F(1s) signals in both mixed SAMs may be due to the presence of defects/pinholes in the SAM. Comparison of both the thickness increases and the intensities of the F(1s) signals of these mixed SAMs suggests that the yield of the reaction carried out by μCP was the same as that by immersion, that is, close to quantitative.[2]

Figure 3 shows a patterned SAM presenting methyl and thiol groups and the subsequent assembly of Au nanoparticles in the regions presenting thiol groups. The patterned SAM was generated by μCP of *n*-hexadecylamine on the reactive SAM followed by reaction with cysteamine ($HSCH_2CH_2NH_2$). Patterned SAMs presenting thiol groups cannot be easily prepared by conventional μCP. The resulting patterned substrate was then immersed in an aqueous suspension of Au nanoparticles stabilized with citrate anions.[14] SEM images show that the Au nanoparticles assembled predominately in the thiol-presenting regions, and the width of the border separating the region having adsorbed nanoparticles from that having none was <100 nm.

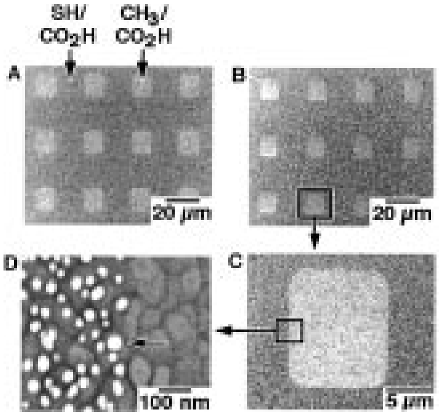

Figure 3. SEM images of (A) a patterned SAM presenting methyl groups (white squares) and thiol groups; (B−D) patterned deposition of Au nanoparticles (white dots pointed by an arrow in D) in the regions that present thiol groups. The background texture in D is the "islands" that are formed on evaporating gold under the conditions we used. The mean diameter of the Au nanoparticles was ~20 nm.

We have also prepared SAMs presenting sulfonates and guanidines by allowing the reactive SAM to react with 3-amino-1-propanesulfonic acid ($H_2N(CH_2)_3SO_3H$) and agmatine sulfate ($H_2N(CH_2)_4NHC(=NH)NH_2 \cdot H_2SO_4$). Patterned SAMs presenting polar and charged terminal groups can be difficult to prepare using conventional μCP.[15] For the SAM-presenting sulfonates, XPS showed a signal at 168.5 eV; we assigned this peak to S(2p) of a sulfonate,[16] and the advancing and receding contact angles of water were both less than 10° (the lowest value we can measure). For the SAM-presenting guanidines, XPS showed an N(1s) signal at 400.4 eV, and the advancing contact angle of water was 47° and the receding contact angle 30°.

The procedure based on a combination of μCP and chemical reaction provides a straightforward method of patterning SAMs on Au and Ag. The key chemical reaction—reaction of amine and surface anhydride—proceeds rapidly in close to quantitative yield, with good edge definition. Although the reaction generates a ~1:1 mixture of *N*-alkyl amides and carboxylic acids on the surface, the carboxylic acid is (at least for large amines) hydrogen bonded to the neighboring carboxylic acids or amides and sterically sheltered by a layer of alkyl groups; it may therefore be largely impeded from interactions with molecules in solution, with the terminal groups on the *N*-alkyl amides, and with molecules of interest adsorbed on the surface. We believe that this method provides a simple and convenient route to patterned SAMs presenting a variety of functional groups—especially polar, charged, or structurally complex groups such as peptides, polymers, and oligosaccharides.

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