

Nanolithography and Nanochemistry utilizing Scanning Probe Techniques: Directed Self-Assembly of Sub-Micrometer-Sized Structures by Scanning Probe Lithography Defined Templates

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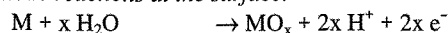
Oxidative scanning probe lithography on octadecyltrichlorosilane monolayers on silicon supports has been used to create well-defined patterns with 20 nm resolution. Due to differences in local surface charges and chemical reactivity these templates have been used in a number of different subsequent chemical modification reactions. Here we report on the directed assembly of monolayers of octadecyl trimethyl ammonium bromide and on the assembly of cationic gold and silica nanoparticles. These structures themselves may again function as templates in a more complex build-up of functional nanostructures, ultimately leading to application in fields as nanosensors and lab-on-a-chip devices.

Key words: Scanning Probe Lithography, Self-Assembly, Nanodevice, Nanochemistry

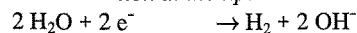
1. INTRODUCTION

Scanning probe lithography was first reported in 1985 by Güntherodt et al. who reported the possibility to create well-defined structures in Pd₈₁Si₁₉ samples.[1] Structure formation was attributed to the polymerization of an adsorbed oil layer originating from the vacuum oil-pumps. The same method proved to be applicable to a broad range of substrates including silicon and metal films.[2] A general reaction scheme for the oxidation was proposed by Sugimura:[3]

Anode reactions at the surface:



Cathode reaction at the tip:



First examples of patterning on organic self-assembled monolayers were reported by U. Heinzmann.[4,5] In this case hexadecanethiol and N-biphenylthiol on Au(111) and octadecyltrichlorosilane (OTS) on Si(100) were utilized.

Following successful lithography experiments using the STM, several groups transferred the oxidation techniques to AFM on substrates as silicon, titanium, tantalum, chromium, organic resists, self-assembled monolayers, and Langmuir-Blodgett films[6] using this technique to create nanometer-sized electronic devices like, for example, constricted titanium nanowires[7] and a single electron MOSFET[8]. In 1999, a variation on the technique was reported by Sagiv et al., who demonstrated the formation of local carboxylic acid functionality by local probe oxidation of monolayers of OTS and 18-nonadecyltrichlorosilane (UTS) on flat silicon substrates.[9] This technique has been used in a number of chemical modification reactions, leading to,

for example, spatially defined, sub-micrometer-sized islands of silver or cadmium sulfide as well as the self-assembly of additional monolayers of OTS and UTS onto templates defined by local probe oxidation processes.[10-12]

Here we report on the application of scanning probe lithography for the preparation of well-defined templates on octadecyltrichlorosilane, which will be used for the specific adsorption of 1) quaternary ammonium salts, 2) cationic gold nanoparticles and 3) silica nanoparticles.

2. RESULTS AND DISCUSSION

Local probe oxidation on OTS-covered monolayers ($\theta_{\text{water}} = 105 - 110^\circ$) was done by moving a conducting, negatively biased (-10 V to -8 V) AFM-tip along a trajectory. Upon contact, top methyl groups of the OTS layer are (partially) oxidized to carboxylic acids. This can be observed by lateral force microscopy imaging (the observed height of an area does not decrease): a clear friction signal appears at the oxidized regions, originating from the increased interaction between the tip and the hydrophilic carboxylic acid groups compared to the methyl end-groups in the unexposed areas.

Figure 1 shows the results for the oxidation of a triangular shaped area. The height of the oxidized area is decreased by only 0.2 nm (Figure 1a) along with a clear signal in the simultaneously recorded friction image (Figure 1b). Upon exposure of the sample to a solution of octadecyltrimethylammonium bromide (OTAB), a second monolayer assembles on top of the oxidized template. Successful assembly of the monolayer can be concluded from an observed increase in the height image of 2 nm, corresponding to the size of the quaternary ammonium salt. Along with the height increase the friction signal disappears, as the top of the assembly

consists of the same end groups as the unoxidized areas. Structures that have been formed in this fashion are stable against washing with water, cleaning with office tape and contact mode AFM-imaging.

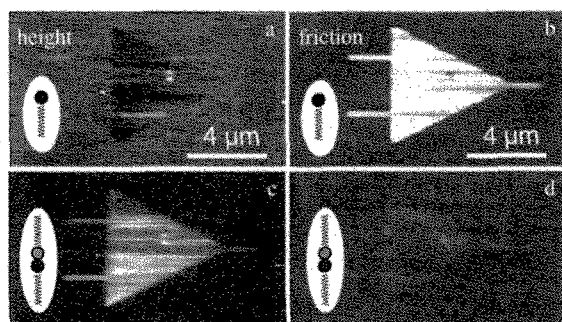


Figure 1. Contact mode AFM images of a scanning probe defined template. Schematic inset represents the formation of local carboxylic acids groups. Left a) height image (z -range 0.5 nm) showing little effect on the height. Right b) LFM image clearly showing successful oxidation by an increased friction signal. After adsorption of octadecyltrimethylammonium bromide the height increases by 2 nm (Left c) and the friction is reduced (d). (Image reprinted with permission from ref. [6], Copyright 2003, the American Chemical Society)

The above mentioned process has been repeated by alternately defining another area, close to the previous one, followed by additional adsorption of OTAB. Figure 2 shows the results after three oxidation – adsorption – washing steps.

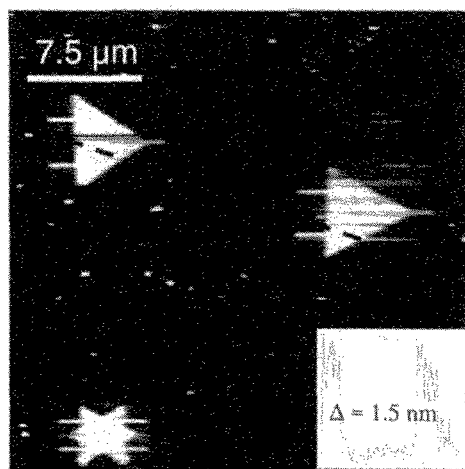


Figure 2. Contact mode AFM image of the sequential oxidation and functionalization. Height increase across the patterns is indicated in the inset. (Image reprinted with permission from ref. [6], Copyright 2003, the American Chemical Society).

Supported by the observation of successful adsorption of the positively charged quaternary ammonium salt we selected cationic gold nanoparticles as the basis for a second modification scheme. Gold nanoparticles ($d = 20$ nm), coated with poly-*l*-lysine, were obtained from British Biocell. Figure 3 shows the formation of an array of gold nanoparticles on a circular template. The presence of the nanoparticles is reflected by an observed

increase in height by 20 nm. Also observable are areas with 6 nm height difference on the oxidized template but in between the gold nanoparticles. These areas are ascribed to the adsorption of free poly-*l*-lysine chains, as no further adsorption of gold nanoparticles was possible on these specific regions. Like for the quaternary ammonium salts, formed structures were stable against washing with water and cleaning procedures with office tape.

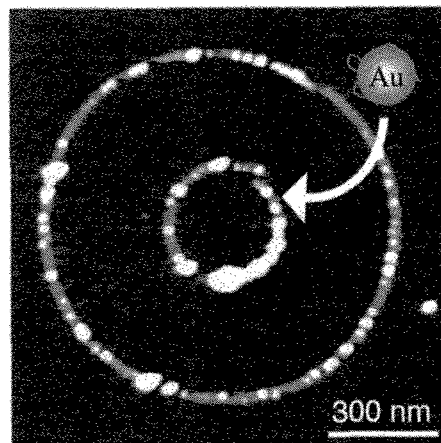


Figure 3. Tapping mode height image ($1.1 \mu\text{m} \times 1.1 \mu\text{m}$, z -range 18 nm) of cationic gold nanoparticles adsorbed to an oxidized structure. The observed height of the particles ranges from 17 to 20 nm. The grey zones in between the particles have 6 nm height. (Image reprinted with permission from ref. [6], Copyright 2003, the American Chemical Society)

Moreover, the oxidized templates can also be used as templates for the adsorption of silica nanoparticles. Because of the effective negative charge on the particles they cannot directly be adsorbed to the surface, an intermediate functionalization step is required. In this step aminopropyltrimethoxysilane (APTS) is attached to the oxidized template. The resulting height increase is negligible but the formed amine functionality on the surface allows for successful coupling of the silica particles as shown in Figures 4 and 5. Figure 4 shows the initial template consisting of a cross and two circles. Next, after addition of APTS, the silica particles ($d = 12$ nm) are added (Figure 5).

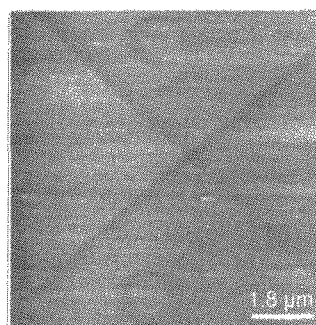


Figure 4. The oxidation template that will be used in the addition of silica nanoparticles shows a decrease in height for the oxidized areas of about 0.5 nm.

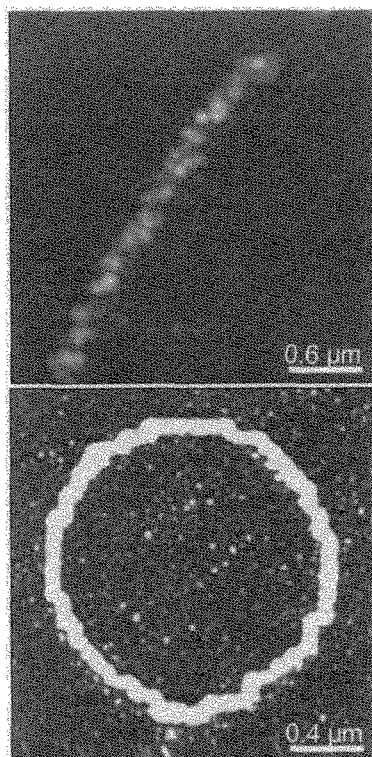


Figure 5. Close-up tapping mode height images of parts of the template from Fig. 4. Observed height of the particles is 10 nm.

Although the attachment of silica nanoparticles was successful, the obtained structures are not as stable as the previously reported ones. The particles are loosely physisorbed on the template and contact mode AFM imaging is sufficient to completely remove the particles from the template. This makes these structures less favorable. The coupling could be strengthened in the case that the amines would be converted to permanent positive charges.

3. OUTLOOK

We demonstrated the possibility to produce well-defined, sub-micrometer-sized templates that can be used in subsequent functionalization schemes. This technique may be used in the formation of, for example, nanometer-sized sensor devices consisting of an array of functionalities coupled to a substrate in a pre-defined format. Work in the direction of coupling proteins to the oxidized templates and using the gold nanoparticles in additional thiol chemistry is currently in progress.

4. EXPERIMENTAL

Experimental details on the formation of OTS monolayers, the probe oxidation processes and the adsorption of quaternary ammonium salts and gold nanoparticles have been published elsewhere.[12]

3-(Aminopropyl)trimethoxysilane was attached to the oxidized template by immersion of the substrate into a APTS solution (1 wt% in water) for 1 h at 100 °C. After cleaning the substrate from excess APTS by rinsing with water and toluene, a drop of a 0.02 wt% solution of silica nanoparticles (Ludox HS-40) was placed on the sample.

AFM imaging was done on a Solver P47H (NT-MDT) using NSG11-type tips. Oxidation was done in contact mode using W₂C-coated tips (CSC12-W2C, NT-MDT).

4. ACKNOWLEDGEMENT

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