Soft and Probe Lithography Without Ink Transfer

Jurriaan Huskens, Xuemei Li, Mária Péter, and David N. Reinhoudt

Laboratory of Supramolecular Chemistry and Technology, MESA+ Institute for Nanotechnology, University of Twente, Enschede, PO Box 217, 7500 AE Enschede, The Netherlands. Phone: +31-53-4892995; fax: +31-53-4894645; E-mail: j.huskens@utwente.nl

ABSTRACT

The present study shows examples of novel strategies for eliminating diffusion as an underlying principle of μCP and DPN. The preparation and use of catalytically active stamps was shown with a catalyst attached directly to the stamp surface. With these stamps it is possible to form patterned SAMs without any transfer of ink. These stamps were more active than the earlier developed oxidized stamps and provide an ink-free μCP scheme allowing more versatile catalytic reactions, and also allow physical and chemical pattern functionalization. Furthermore, an extension to catalytic probe lithography was given. Here line patterns with sub-100 nm widths were created by scanning a catalyst-functionalized tip across a reactive SAM substrate.

Keywords: nanotechnology, soft lithography, microcontact printing, probe lithography, self-assembled monolayers
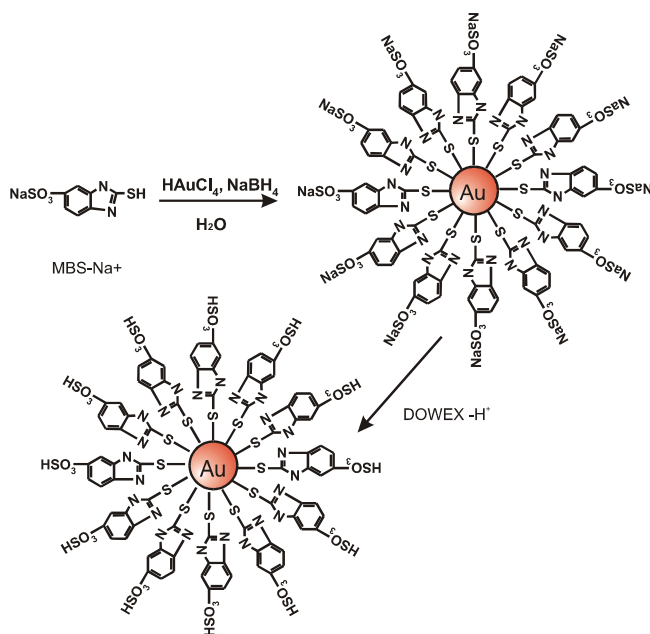
1 INTRODUCTION

Microcontact printing [1] (μCP) is a versatile technique for the creation of patterned surfaces. It commonly employs the transfer of an ink (e.g. a thiol) onto a surface (e.g. a gold-coated substrate) thus forming a self-assembled monolayer (SAM). Patterns of different thiols can be created using self-assembly of a second thiol from solution, or the printed patterns can be used directly as etch resists allowing the structuring of the underlying substrate itself. This technique has been extended to probe lithography in the recently developed dip-pen nanolithography (DPN) [2].

Resolution of these techniques is typically around 200 nm, diffusion of the ink during the printing or writing stage being the main limiting factor [3]. Diffusion can be restricted when heavy inks are used, such as high-molecular-weight thioethers [4], proteins [5], or nanoparticles [6]. The present study will show examples of novel strategies for eliminating diffusion as an underlying principle of μCP and DPN.
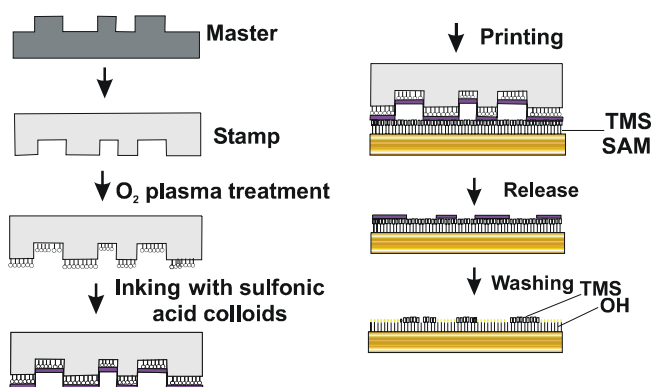
2 RESULTS AND DISCUSSION

2.1 Microcontact Printing with Catalytically Active Nanoparticles

Microcontact printing with nanoparticles leads to well-defined patterns because of the lack of diffusion of the printed particles [6]. For the same reason, however, the order of the printed particle pattern is usually poor and does not provide etch resistance. In order to obtain well-ordered, patterned SAMs but at the same time keep the advantage of diffusion-less printing of nanoparticles, we have coated gold nanoparticles with catalytically active acid groups (Scheme 1) to hydrolyze protecting silyl ether (either trimethylsilyl, TMS, or tert-butyl-dimethylsilyl, TBDMS) groups present at a homogeneous SAM when transferred onto this SAM by μCP (Scheme 2) [7]. This has led to patterned SAMs with an edge resolution below 100 nm (Figure 1).

Scheme 1. Preparation of catalytically active gold nanoparticles.

Scheme 2. General μCP scheme for printing catalytically active gold nanoparticles onto a reactive SAM.
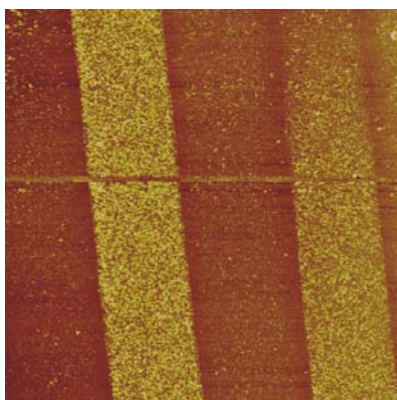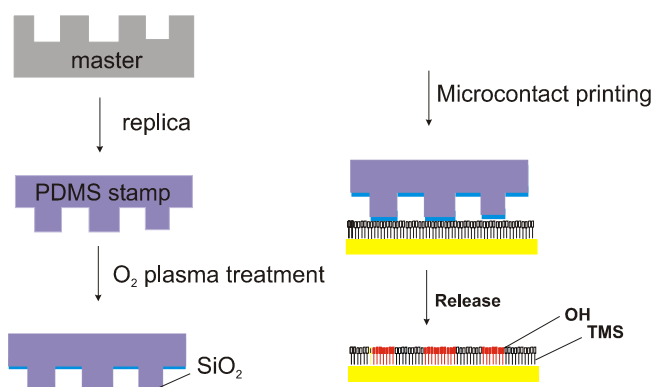

Figure 1. An AFM phase image (30×30 μm^2) of a TMS SAM patterned by μCP with catalyst-functionalized gold nanoparticles (bright areas: TMS, dark areas: hydrolyzed TMS).

2.2 Microcontact Printing with Oxidized Stamps

Ideally, in order to completely eliminate diffusion as the underlying principle of μCP, one could envisage pattern formation without the transfer of ink but rather by contact of the stamp with a substrate only. This idea was pursued by using oxidized PDMS stamps that can catalytically cleave silyl ether groups of reactive SAMs in an ink-free μCP process (Scheme 3) [8]. Pattern formation on both TMS and TBDMS (Figure 2) SAMs was shown to occur with sub-100 nm edge resolution. On the former, more reactive SAMs, pattern formation was achieved in only a few min of contact, whereas for the latter SAMs contact times needed to be above 10 min to be visible by AFM.
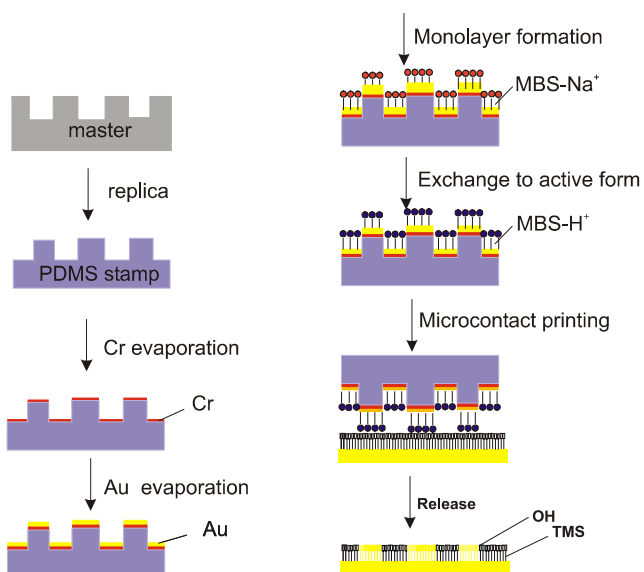

Scheme 3. General μCP scheme for printing with catalytically active, oxidized PDMS stamps onto a reactive SAM.

Figure 2. An AFM friction image (25×25 μm^2) of a TBDMS SAM patterned by μCP with oxidized PDMS stamps (dark areas: TBDMS, bright areas: hydrolyzed TBDMS).

2.3 Microcontact Printing with Catalyst-Functionalized Stamps

In order to achieve more active stamps, a catalyst was attached directly to the surface of a gold-coated PDMS stamp (Scheme 4). With these stamps it was possible to form patterned SAMs without any transfer of ink (Figure 3). These stamps were more active than the earlier developed oxidized PDMS stamps. Such a general approach for attaching catalysts to a stamp in principle provides an ink-free μCP scheme allowing more versatile catalytic reactions as well.

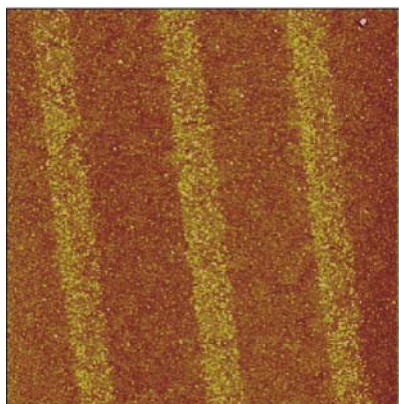**Scheme 4.** General μCP scheme for printing with catalyst-functionalized PDMS stamps onto a reactive SAM.

Figure 4. An AFM height image (25×25 μm^2) after adsorption of amino-functionalized polystyrene nanoparticles (height 120 nm) onto a SAM patterned by μCP with an OH thiol (narrow areas) and filling with a TMS adsorbate (wide areas).

Figure 3. An AFM friction image (25×25 μm^2) of a TMS SAM patterned by a catalyst-functionalized PDMS stamp (bright areas: TMS, dark areas: hydrolyzed TMS).

2.4 Pattern Enhancement

The versatility of the current schemes employing TMS and TBDMS SAMs was shown by using such patterned SAMs in guided deposition of nanoparticles by physisorption and in pattern enhancement by chemical functionalization. Amino-functionalized polystyrene nanoparticles (120 nm diameter) were deposited from solution onto a patterned SAM with TMS- and OH-functionalized areas created by μCP. The particles showed a large preference for adsorption onto the OH areas forming a layer with a single-particle thickness (Figure 4), probably owing to the formation of multiple hydrogen bonds. Versatile chemical functionalization of patterned TBDMS SAMs was possible using reaction with a diisocyanate, followed by an amine (Scheme 5). Also this approach showed preferential reaction of the OH areas (Figure 5), in this case because the TBDMS groups are protecting the other SAM areas.
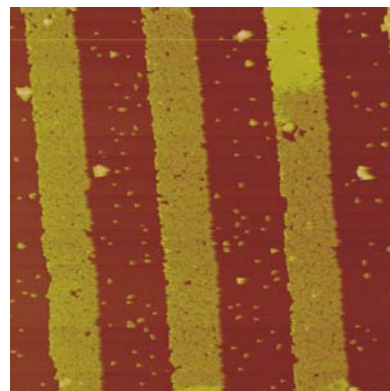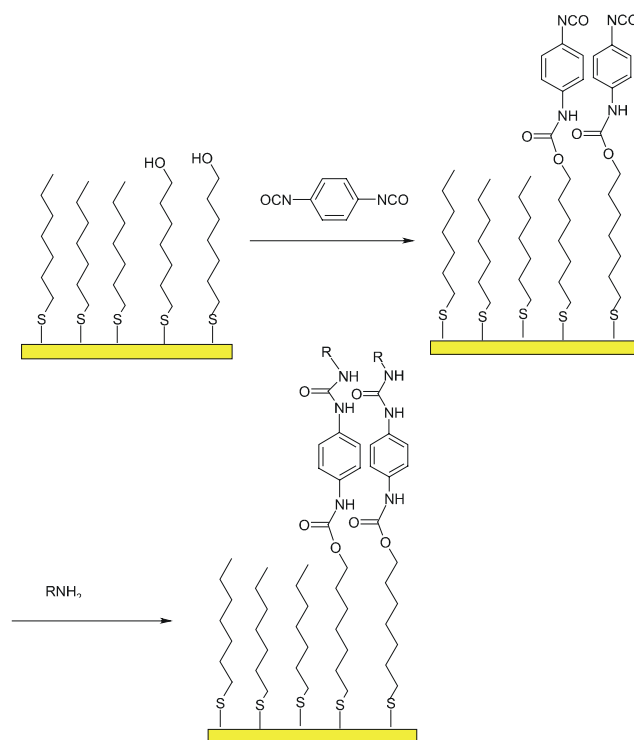

Scheme 5. Chemical amplification of patterned SAMs by reaction of exposed OH functionalities.

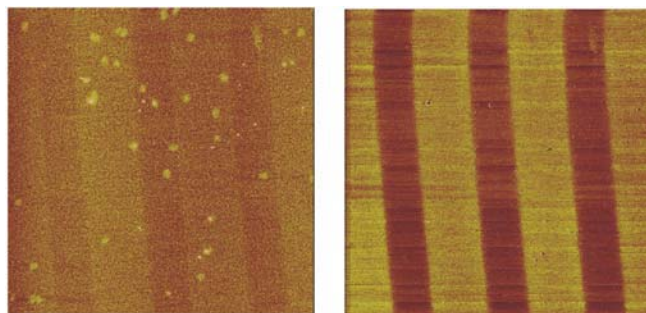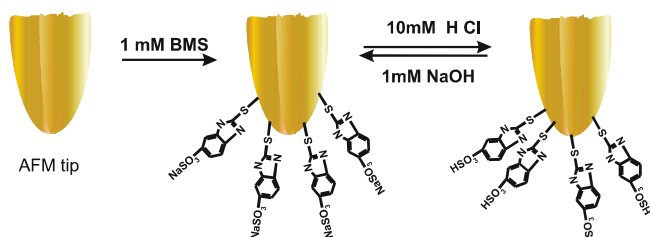**Figure 5.** AFM height (left) and friction (right) images (25 × 25 μm^2) after reaction of the OH-functionalized areas of a SAM patterned by μCP with an OH thiol (wide areas) and filling with a TBDMS adsorbate (narrow areas).

2.5 Catalytic Probe Lithography

The catalytic μCP process shown in Scheme 4 was extended to catalytic probe lithography by using catalytically active AFM tips instead. Hereto, gold-coated AFM tips were functionalized with an acid catalyst (Scheme 6). Scanning such a catalytically active tip across a reactive TMS SAM substrate led to hydrolysis of the TMS groups in the contacted areas as shown by higher friction (Figure 6, left). Sub-100 nm lines were written as well (Figure 6, right).

Scheme 6. Functionalization of gold-coated AFM tips with an acid catalyst.
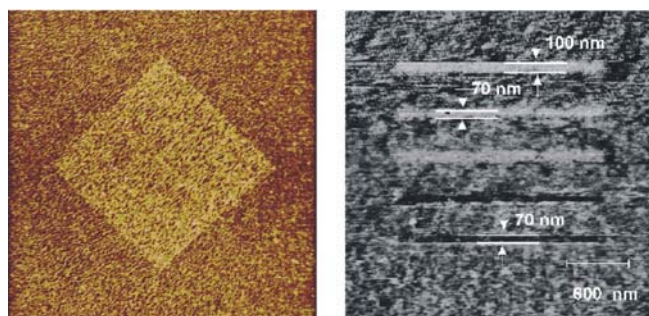

Figure 6. AFM friction images of box (left, 6 × 6 μm^2) and line patterns with sub-100 nm widths (right, 3 × 3 μm^2) created on TMS SAMs by catalytic probe lithography using an acid-functionalized AFM tip (bright box and lines: with an active tip, dark lines: with an inactive tip).

3 CONCLUSIONS

Catalytic schemes have been developed for μCP and probe lithography. Not only can such schemes lead to improved resolution because of the complete elimination of diffusion, but they may also lead to more versatile nanofabrication schemes in general.

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