Sulfonic Acid-Functionalized Gold Nanoparticles: A Colloid-Bound Catalyst for Soft Lithographic Application on Self-Assembled Monolayers

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Abstract: In this report, we present a new lithographic approach to prepare patterned surfaces. Self-assembled monolayers (SAMs) of the acid-labile trimethylsilyl ether $(TMS-OC_{11}H_{22}S)_2$ (TMS adsorbate) was formed on gold. 5-Mercapto-2-benzimidazole sulfonic acid sodium salt $(MBS-Na^+)$ was used as a ligand for gold nanoparticles. These monolayer-protected gold colloids (MPCs) were transformed into the catalytically active H^+-form by ion exchange. This colloid-bound catalyst hydrolyzed the TMS adsorbate $(TMS-OC_{11}H_{22}S)_2$ both in solution and when self-assembled on gold surfaces. Microcontact printing of the active colloid-bound catalyst on the preformed TMS SAM led to the deposition of the colloid onto the SAMs. After the catalyst nanoparticles were rinsed off, a patterned surface was created as shown by AFM.

Introduction

Self-assembled monolayers (SAMs) on gold are attractive for the development of sensors,[1,2] interfaces,[3] and for nanofabrication.[4−6] Recently, such SAMs have been applied for the generation of well-defined patterns on the micro/nanometer scale. These patterned SAMs can be used as resists for pattern transfer[7] and as templates for patterning proteins and other biosystems.[8,9]

Patterned SAMs can be created by various direct techniques such as UV-photolithography, e-beam lithography, and by replication techniques, such as microcontact printing (μCP).[10,11] Microcontact printing can be conducted routinely in the lab without the need of cleanroom equipment, and it is compatible with a wide range of surface functional groups, including the structurally complex and fragile groups found in biology and biochemistry.[12] The substrate used for printing is not limited to flat surfaces, thus rendering this technique a versatile tool for chemical patterning.

Microcontact printing employs an elastomeric stamp to transfer ink (alkanethiols) to a substrate via conformal contact. It has been widely used to create patterned SAMs on gold because alkanethiols give a strong interaction with gold and form robust SAMs in the contacted areas. The microcontact printing process depends on various factors to attain reliable and reproducible results. Stamp materials need to be elastomeric to allow conformal contact and show little adhesion for easy release after printing. The most widely used material is poly-(dimethylsiloxane) (PDMS). Second, long chain alkanethiols have been used as the ink because they form densely packed, etch resistant SAMs. Other factors such as printing time and inking method are also important.[13]

Microcontact printing relies on ink diffusion from stamp to substrate, and this imposes limitations on the resolution that can be attained. Several ink transfer pathways have been identified which led to the undesired ink transport to the noncontacted areas, for example, by vapor phase deposition and ink diffusion along the surface.[14] Such processes may be restricted by the use of heavier inks.[15] Macromolecules such as proteins have also been used as the ink.[16] Even palladium nanoparticles have been transferred, which initiated metallization of copper as shown by Whitesides et al.[17,18] They showed that patterns were faithfully transferred without diffusion, indicating that nanoparticles are of potential use as ink for microcontact

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printing. Potential problems with printing nanoparticles lie in the control of the amount and order of materials transferred. We envisage the use of catalytic nanoparticles to prepare patterned SAMs, thus avoiding those problems while retaining the aforementioned advantages of using nanoparticles as the ink.

Here we describe the preparation of sulfonic acid derivatized monolayer-protected gold nanoparticles (MPCs) and their application as a catalyst to hydrolyze a trimethylsilyl ether (TMS) adsorbate. The reactivity of this colloid-bound catalyst was investigated in the hydrolysis of this TMS adsorbate both in solution and when self-assembled on gold. The MPCs were further used as an ink for microcontact printing on the preformed TMS SAMs. Local hydrolysis of the TMS adsorbate molecules is shown to be a novel method for pattern creation.

Experimental Section

Chemicals. All chemicals were used as received, unless otherwise stated. $HAuCl_4 \cdot xH_2O$ (99.99%) was purchased from Acros Organics, tetraoctylammonium bromide from Fluka. DOWEX-H$^+$ ion-exchange resin was purchased from Janssen Chimica. 11-Mercapto-1-undecanol (MUD), 5-mercapto-2-benzimidazole sulfonic acid sodium salt (MBS-Na$^+$), and trimethylsilyl chloride (TMS-Cl) were purchased from Aldrich. Silver enhancer was obtained from Sigma. Water was purified by Millipore membrane units. Solvents for colloid preparation were reagent grade. Solvents used for organic synthesis were purified according to standard laboratory methods.[19]

Bis(ω-trimethylsiloxyundecyl)disulfide ((TMS-OC$_{11}$H$_{22}$S)$_2$). To 11-mercapto-1-undecanol (1.0 g, 4.89 mmol) in dichloromethane (50 mL) was added iodine (0.5 g, 3.10 mmol). The solution was stirred overnight. The reaction mixture was washed twice with 1 M aqueous NaS_2O_3 and twice with water, and subsequently dried over Na_2SO_4. After the solvent was removed, bis(ω-hydroxyundecyl)disulfide was obtained in a quantitative yield as a white solid. ^{1}H NMR (CDCl$_3$) δ (ppm): 3.65 (t, 4H, $J = 7.6$ Hz), 2.70 (t, 4H, $J = 4.3$ Hz), 1.50–1.75 (m, 8H), 1.20–1.40 (m, 28H). To a solution of this disulfide (200 mg, 0.50 mmol) in dry THF (50 mL) were added TMSCl (133 mg, 1.25 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (164 mg, 1.10 mmol). The reaction mixture was stirred overnight under argon. After the precipitate was filtered off from the reaction mixture, the solution was washed twice with water and dried over Na_2SO_4. After the solvent was removed and dried under vacuum, (TMS-OC$_{11}$H$_{22}$S)$_2$ was obtained as an oil (0.24 g, 90%). ^{1}H NMR (CDCl$_3$) δ (ppm): 3.57 (t, 4H, $J = 6.6$ Hz), 2.68 (t, 4h, $J = 7.3$ Hz), 1.43–1.72 (m, 8H), 1.24–1.37 (m, 28H), 0.11 (s, 18H). MS (FAB-MS) m/z: 550.7 ([M]$^+$; calcd. for $C_{28}H_{62}O_2S_2Si_2$: 551.1).

MBS-Na$^+$-Functionalized Gold Nanoparticles (Na$^+$-MPCs). An aqueous solution (7 mL) of MBS-Na$^+$ (126 mg, 0.50 mmol) was added to tetrachloroauric acid (100 mg, 0.29 mmol) in water (3 mL). The reduction was carried out by dropwise addition of freshly prepared sodium borohydride (130 mg, 3.50 mmol) in water (20 mL) at a rate of approximately 0.3 mL/min while stirring. The nanoparticles were formed instantaneously as witnessed by the color change to dark brown. The solution was stirred at room temperature for 2 h. Na$^+$-MPCs were lyophilized after filtering. The black solid was suspended in methanol (150 mL) at −18 °C for 4 h and re-collected by centrifugation, followed by washing with methanol (3×). To remove water-soluble byproducts, Na$^+$-MPCs were further purified by dialysis and dried under vacuum, yielding a black solid (30 mg, 52%). ^{1}H NMR in D$_2$O showed no free MBS ligands, only broadened resonances for the MPC-attached MBS. IR: $\nu = 3419$ (NH), 1625 (C=C, C=N), 1140 (O=S=O), 1087 (O=S=O) cm^{-1}.

MBS-H$^+$-Functionalized Gold Nanoparticles (H$^+$-MPCs). Na$^+$-MPCs (30 mg) were dissolved in water (10 mL). The pH of the colloid solution was neutral. This solution was passed over a DOWEX-H$^+$ ion-exchange column. The pH of the solution decreased to 2. Water was removed by lyophilization, giving a black, hygroscopic solid.

Hydrolysis of TMS Adsorbate by H$^+$-MPCs in Solution. The TMS adsorbate (10 mg) was dissolved in CDCl$_3$. A catalytic amount of H$^+$-MPCs (~1 mg in CD$_3$OD) was then added. A ^{1}H NMR spectrum was taken directly, which showed that the cleavage was complete. ^{1}H NMR (CDCl$_3$) δ (ppm): 3.65 (t, 4H, $J = 7.6$ Hz), 2.70 (t, 4H, $J = 4.3$ Hz), 1.50–1.75 (m, 8H), 1.20–1.40 (m, 28H). MS (FAB-MS) m/z: 407.4 ([M + H]$^+$; calcd. for $C_{22}H_{46}O_2S_2$: 406.3).

Monolayer Preparation. All glassware used for monolayer preparation was immersed in piranha (concentrated H_2SO_4 and 33% aqueous H_2O_2 in a 3:1 ratio; warning: Piranha should be handled with caution; it has been reported to detonate unexpectedly) and rinsed with large amounts of water (Millipore). Nearly atomically flat gold substrates were obtained from Holland Biomaterials Group BV (Enschede, The Netherlands) as a layer of 20 nm gold on titanium (2 nm) on silicon. Before use, the substrates were treated with oxygen plasma (5 min) and ethanol (5 min). After being rinsed, the substrates were directly immersed into the adsorbate solution. Self-assembled monolayers (SAMs) were prepared by immersing the freshly cleaned gold substrates in a 1 mM TMS adsorbate solution at room temperature for 14 h. The SAMs were rinsed by chloroform, ethanol, and water, and dried under a stream of nitrogen.

Contact Angle Measurements. Water contact angles were measured on a Krüss G10 contact angle goniometer, equipped with a CCD camera. The advancing and receding contact angles were measured during the growth and shrinkage of a droplet, respectively.

Microcontact Printing (μCP). PDMS stamps were prepared according to a published procedure.[20] To allow application of aqueous ink solutions, they were treated with an O$_2$ plasma for 15 s.[17] No treatment was required when methanolic solutions were used, that is, a H$^+$-MPC solution. The (pretreated) PDMS stamp was inked with the gold nanoparticle solution and blown dry under a stream of nitrogen; this procedure was repeated two or three times. The stamp was then brought into contact with the SAM substrate for 5 min. After the stamp was released, the surface was rinsed with large amounts of methanol and water. Alternatively, the substrates were treated with silver enhancer,[21] which enlarges the colloidal gold by electroless deposition of metallic silver to give a high contrast. The silver enhancer kit consists of solution A (silver salt), solution B (initiator), and sodium thiosulfate (fixer). In brief, solution A and solution B were mixed 1:1 immediately before use and applied to the SAM with the gold colloidal particles. After 5–10 min, the substrate was rinsed with water, fixed 2–3 min in a sodium thiosulfate solution, and rinsed again.

FT-IR. Infrared spectra were collected by pressing the MPCs into KBr pellets and using KBr as the background on a Perkin-Elmer FT IR BX system.

XPS. X-ray spectroscopy was collected from a Quantum 2000 Scanning Esca Microprobe; the Quantum 2000 uses a Quartz crystal monochromator and a scanning electron source that excites the aluminum anode to produce a focused X-ray beam. The created photoelectrons pass through a Spherical Capacitor Energy Analyzer and are detected with a MultiChannel Detector (16 channels). Surface survey data were collected followed by high-resolution scans over C1s (278–298 eV), O1s (525–545 eV), S2s (222–242 eV), and Si2s (145–165 eV). Peak areas were calculated using the Gaussian fit program. Relative peak area ratios were calculated according to published results.[22]

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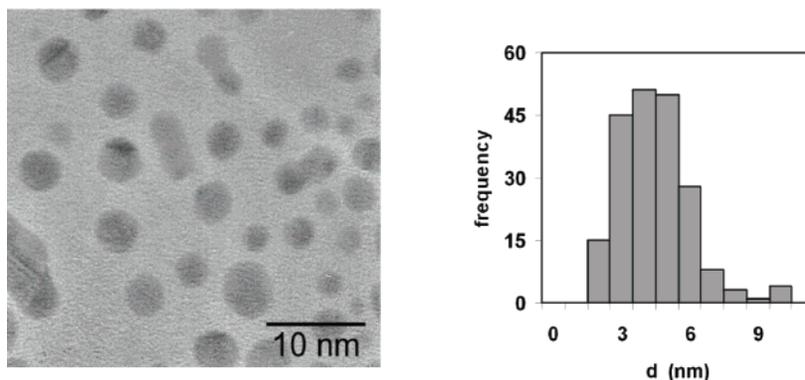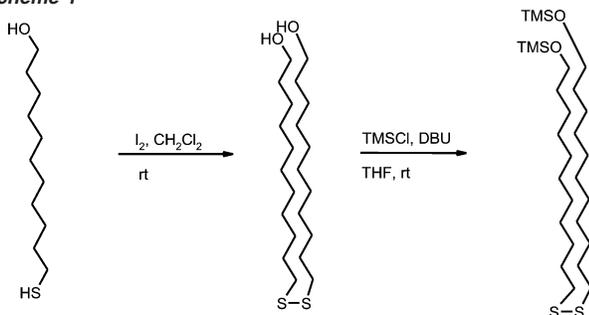
Figure 1. A transmission electron microscope (TEM) image and the size histogram of the Na$^+$-MPCs.

Scheme 1

TEM. Transmission electron microscopy (TEM) images were collected on a Philips CM 30 Twin STEM, fitted with Kevex delta plus X-ray dispersive electron spectroscopy (EDX) and Gatan model 666 PEELs, operating at 300 kV. Samples were prepared by drop-casting a drop of gold colloid dichloromethane solution onto a 200 mesh copper grid and were left to dry for 10 min.

NMR. NMR spectra were recorded at 25 °C using a Varian Inova 300 spectrometer. ^{1}H NMR chemical shifts (300 MHz) are given relative to residual CHCl$_3$ (7.25 ppm) as an internal standard. ^{13}C NMR chemical shifts (75 MHz) are given relative to CDCl$_3$ (77.0 ppm).

FAB-MS. Mass spectra were recorded with a Finnigan MAT 90 spectrometer using NBA/NPOE as a matrix.

AFM. Tapping mode AFM images were acquired in air on a Nanoscope III instrument.

Results and Discussion

Trimethylsilyl (TMS) ethers are widely used as protective groups for organic synthesis. They are labile to acid or base hydrolysis, but acid stability is quite dependent on the local steric environment.[23] Bis(ω-trimethylsiloxyundecyl)disulfide ((TMS-OC$_{11}$H$_{22}$S)$_2$, TMS adsorbate) was synthesized as shown in Scheme 1. 11-Mercapto-1-undecanol (MUD) was oxidized to the disulfide by iodine in a quantitative yield. The disulfide was then turned into the TMS adsorbate by reaction with trimethylsilyl chloride (TMS-Cl).

5-Mercapto-2-benzimidazole sulfonic acid sodium salt (MBS-Na$^+$) was used as a protecting ligand in gold nanoparticle preparation. The monolayer-protected gold nanoparticles (MPCs)

were made in a one-phase system (water) by the reduction of hydrogen tetrachloroaurate using sodium borohydride in the presence of MBS-Na$^+$ (Scheme 2). Fast addition of the reducing agent gave a black precipitate. Soluble Na$^+$-MPCs were obtained only when the reduction was carried out at an addition rate of 0.3 mL/min or slower. The gold nanoparticles were purified by precipitation from methanol, giving a gray-black solid. The Na$^+$-MPCs were water soluble, stable in air, and were dried and redissolved without change. The IR spectrum of the Na$^+$-MPCs resembles that of MBS-Na$^+$, which confirmed the presence of the ligands on the colloids. The absence of a thiol absorption band in the Na$^+$-MPCs spectrum indicates the absence of free MBS ligand in the colloids. The presence of the sulfonate functionality is further evidenced by O=S=O stretching vibrations at 1140 and 1086 cm^{-1}. The ^{1}H NMR spectrum showed line broadening as compared to MBS-Na$^+$ and again the absence of free MBS-Na$^+$. UV/vis showed a typical surface plasmon absorbance of gold (520 nm). The particle size (4.0 ± 1.5 nm) was determined by TEM (Figure 1).[24] A significant number of particles exhibiting twinning and preferential {111} surface facet planes are clearly visible, which was also observed by others.[25]

Exchange to the catalytically active H$^+$ form (H$^+$-MPCs) was achieved by passing an aqueous solution of the Na$^+$-MPCs over a DOWEX-H$^+$ ion-exchange resin column (Scheme 2). The pH value of the colloid solution after treatment was around 2. These colloids were soluble both in water and in methanol.

Hydrolysis in Solution. To probe the catalytic activity, H$^+$-MPCs were tested as a catalyst in solution. The TMS adsorbate was dissolved in CDCl$_3$. A catalytic amount of H$^+$-MPCs ($\sim$1 mg in CD$_3$OD) was then added. A ^{1}H NMR spectrum taken directly after addition showed that the cleavage was complete. This was confirmed by FAB mass spectroscopy. Thus, it was concluded that the colloid-bound catalyst on the H$^+$-MPCs is an active catalyst in the hydrolysis of TMS.

Since the introduction of the two-phase preparation of self-assembled monolayer-protected gold colloids (MPCs) by Brust et al.,[26] a variety of MPCs with desired functionalities has been prepared.[25,27,28] The ligands on the particles bind in the same

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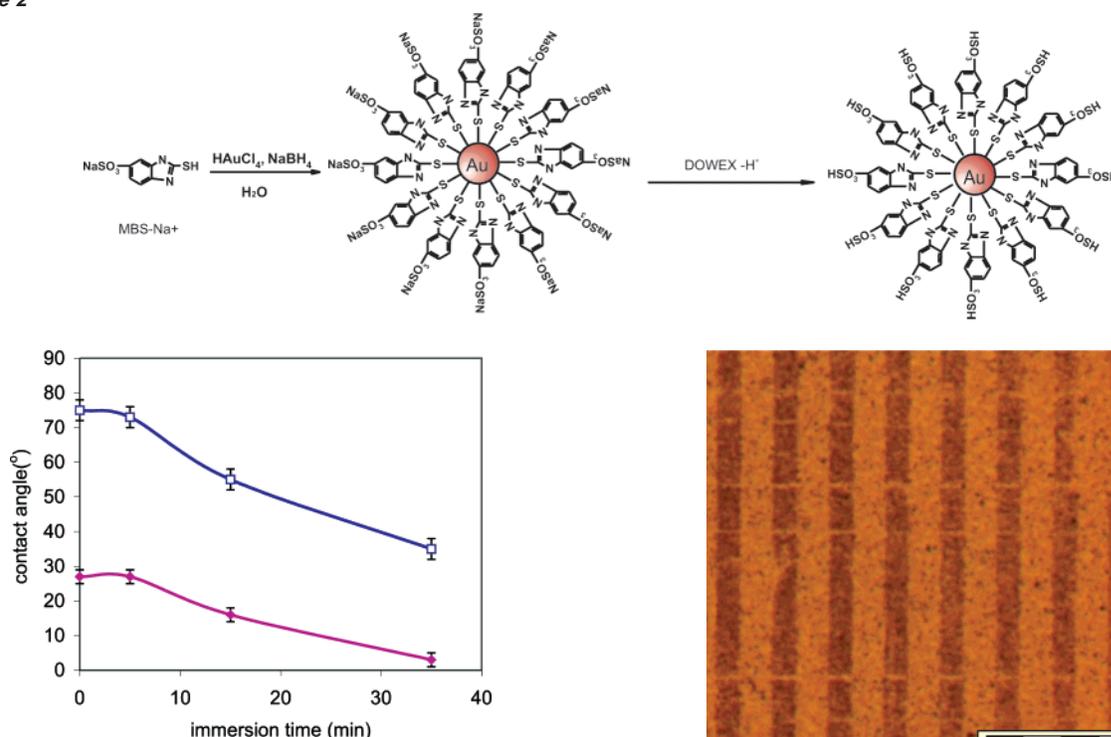
Scheme 2

Figure 2. Advancing (□) and receding (◆) contact angles of a TMS adsorbate monolayer versus the immersion time in a H$^+$-MPC methanol solution.
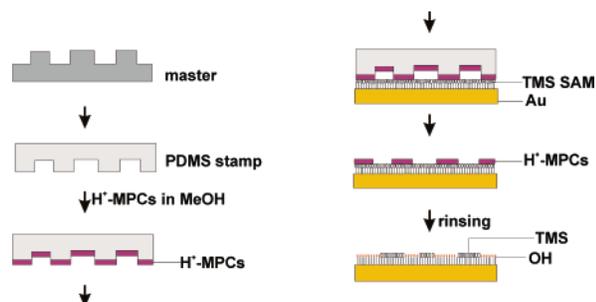

Figure 3. Procedure for the selective hydrolysis of a TMS adsorbate SAM on gold by microcontact printing of H$^+$-MPCs. A PDMS stamp is inked with a solution of H$^+$-MPCs. The stamp is then brought into contact with a TMS adsorbate SAM. After release of the stamp from the surface and rinsing off the nanoparticles, a patterned surface is created.

way as on flat gold surfaces,[29] thus serving as a perfect model for surface reactions at SAMs. Tremel et al.[30] used an ω-functionalized alkanethiol as a capping ligand for gold nanoparticles, and treatment with RuCl$_3$ gave a ring-opening metathesis catalyst. Frigeri et al.[31] prepared *N*-methylimidazole-functionalized MPCs and used these as a catalyst for the cleavage of 2,4-dinitrophenyl acetate. In both studies, the colloid-bound catalysts were applied in solution only.

Hydrolysis on a SAM Surface. Surface−surface reactivity tests were carried out to investigate the applicability of the catalyst in surface patterning. Hydrolysis of self-assembled (3-
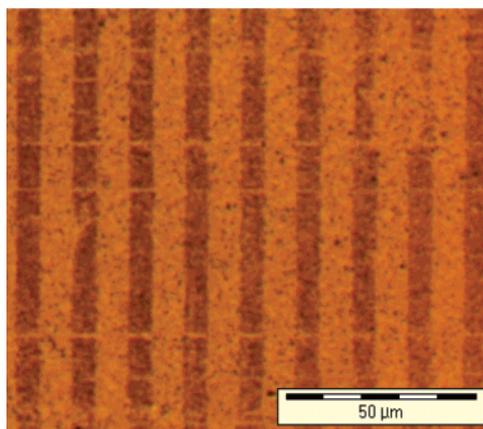
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Figure 4. An optical microscopy image of a TMS SAM substrate after μCP of H$^+$-MPCs followed by silver enhancement (see text).

mercaptopropyl)trimethoxylsilane on gold has been investigated by Pemberton et al.[32] They have used XPS and Raman spectroscopy to quantify the reaction yield. So far, very little is known about the hydrolysis of surface-bound silyl ethers.

SAMs were prepared by immersing gold substrates in a 1 mM solution of the TMS adsorbate in chloroform overnight. The water contact angles of the SAMs were determined to be 75 ± 2° (advancing) and 27 ± 2° (receding).[33] Hydrolysis was carried out by dipping SAM substrates into H$^+$-MPCs in methanol (0.25 g/L) for varying periods of time and was monitored by contact angle goniometry and X-ray photoelectron spectroscopy (XPS).

Grazing incidence angle FT-IR of the TMS SAM showed CH$_2$ vibration at 2920 cm^{-1} (ν_{as}) and 2854 cm^{-1} (ν_s), indicating a crystalline well-ordered nature of the SAM. Vibrations of methyl groups on silicon atoms are expected to appear around 1255−1270 cm^{-1}. However, this peak becomes obscured due to the water absorbance. Thus, it is not reliable to use FT-IR for studying the hydrolysis process.

Contact angle changes are shown in Figure 2. These results show that the SAMs became more hydrophilic upon prolonged contact with the gold nanoparticle solution, which is attributed to the hydrolysis of TMS moieties. The slow hydrolysis rate with the H$^+$-MPCs in solution is attributed to the good solubility of the colloids and thus to the little actual contact time between catalyst and reactive surface groups.

XPS was used to further analyze the hydrolysis of TMS at the surface. Three layers were compared: an intact TMS layer,

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(33) The significant hysteresis might be due to the bulkiness of the TMS moiety and gauche defects as mentioned in ref 32.
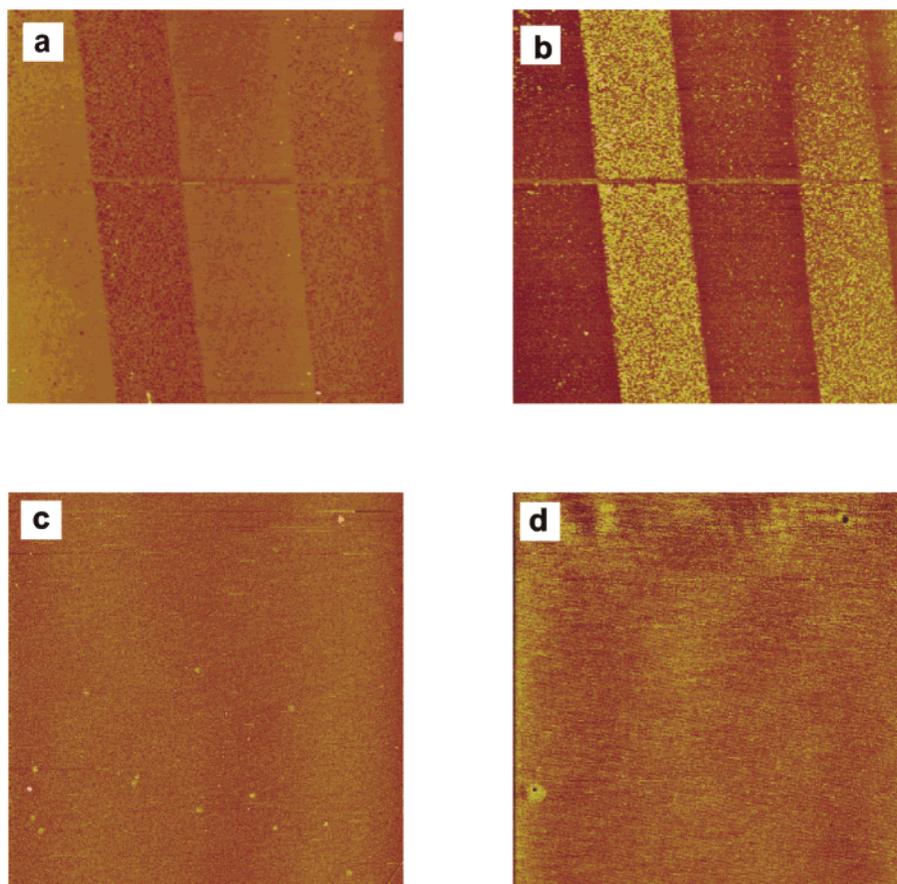
Figure 5. Tapping mode AFM images of TMS adsorbate SAMs after μCP of H$^+$ or Na$^+$-MPCs and thorough rinsing: (a) height image (z range 20 nm) and (b) phase image (z range 40°) after μCP of H$^+$-MPCs (image size: 30 × 30 μM^2); (c) height image (z range 20 nm) and (d) phase image (z range 30°) after μCP of Na$^+$-MPCs (image size: 50 × 50 μM^2).

a TMS layer after 30 min of contact with a H$^+$-MPC solution, and a reference MUD SAM. The concentration of Si in the layer is indicative of the presence of the TMS moieties. The atomic concentration of Si on the intact TMS SAM was 5.2 ± 0.6%, while the reference SAM did not show any Si at all. The TMS SAM which had been in contact with H$^+$-MPCs for 30 min showed 3.4 ± 0.9% of silicon, indicating partial hydrolysis of the SAM, thus confirming the contact angle data.

Microcontact Printing (μCP) of MPCs onto SAMs. μCP employs ink transfer from an elastomeric stamp to a solid substrate by conformal contact. Here, we did not transfer an adsorbate ink, but rather a catalyst which reacts with an already present, densely packed, reactive SAM. The process is illustrated in Figure 3. For application of an aqueous solution of Na$^+$-MPCs, the stamp was made hydrophilic by treatment with an oxygen plasma for 15 s. For application of H$^+$-MPCs in methanol, untreated stamps were used. The stamp was inked with a Na$^+$ or H$^+$-MPC solution, dried under a stream of nitrogen, and then put into contact with the TMS adsorbate SAM. After release of the stamp after 5 min,[34] the substrate was either rinsed thoroughly or put in a silver enhancer solution (Figure 3).

The MPCs could be visualized by optical microscope after microcontact printing on TMS SAM. However, the contrast was not very high. To facilitate the optical visualization of the printed nanoparticles on surfaces, a pattern amplification method was

used in which silver ions were reduced by hydroquinone to silver metal at the surfaces of the gold nanoparticles. Silver enhancement has been used to visualize protein-, antibody-, and DNA-conjugated gold nanoparticles in histochemical electron microscopy studies.[21] An optical microscopy image (Figure 4)[35] confirmed that the colloids (H$^+$-MPCs) had been transferred faithfully.

Alternatively, the MPCs were rinsed off after printing. Tapping mode AFM was used to image the surfaces (Figure 5). The substrate which had been in contact with the H$^+$-MPCs showed replication of the stamp pattern into the SAM. This pattern was barely visible in the height profile of the image (Figure 5a). The phase image (Figure 5b), however, showed a high contrast. We attribute the patterns to alternating areas of unreacted TMS functionalities and hydrolyzed, thus OH-terminated, functionalities at the outer face of the SAM, caused by hydrolysis of the TMS groups by the catalytically active H$^+$-MPCs in the contacted area. The accurate replication of the stamp feature sizes indicates that the nanoparticles have not diffused away from the printed area during the, for normal μCP, long printing times and that catalysis happened only locally in the contacted area.

In a control experiment, μCP of the Na$^+$-MPCs was performed on a TMS SAM surface. The particles were transferred to the TMS SAM according to optical microscopy. After the

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(34) Shorter contact times do not lead to observable patterns on TMS SAMs.

(35) Oxygen plasma treatment created cracks on the stamps as found by: Chua et al. *Appl. Phys. Lett.* **2000**, *76*, 721−723.

particles were rinsed off, AFM imaging did not show any pattern formation on the surfaces (Figure 5c and 5d). This proves that the catalytic activity of the H$^+$-MPCs is essential for pattern replication.

μCP has been used for the transfer of a catalytic palladium colloid, which initiated metallization of copper as shown by Whitesides.[17,18] Here we have shown that catalytic nanoparticles can be transferred by μCP onto a chemically active SAM surface. This catalyst has selectively and locally catalyzed the TMS adsorbate, providing patterns on the SAM surface. The liberated OH functional groups generated in this way may be utilized for further surface modification.

Conclusions

Microcontact printing of a catalytically active species is for the first time performed on a preformed, densely packed, and chemically active TMS SAM. The catalyst was immobilized on colloidal gold, which was used as an ink in microcontact printing. The colloid-bound catalyst proved to hydrolyze the TMS adsorbate in solution as well as when self-assembled on gold. By using μCP, the colloid-bound catalyst was transferred to a TMS adsorbate SAM, which hydrolyzed the TMS adsorbate in the contacted areas, providing patterns with different functional groups. The advantage of printing nanoparticles with μCP is that no diffusion occurs upon transfer as shown before,[17] thus allowing in principle more accurate pattern transfer than normally in μCP, which relies on adsorbate diffusion from the stamp interior to the surface. Scanning force microscopy (SPM) has proven to be a new tool for pattern creation in the nanometer range.[36–42] We expect to use the present system and apply it to SPM lithography, using an AFM tip modified with such a catalyst for writing chemical patterns on reactive SAMs.

Supporting Information Available: XPS and IR results (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0271431

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