DOI: 10.1002/anie.200801013

Surface Patterning

Local Probe Oxidation of Self-Assembled Monolayers: Templates for the Assembly of Functional Nanostructures

*Daan Wouters, Stephanie Hoeppener, and Ulrich S. Schubert**

monolayers · nanostructures ·
scanning probe microscopy · self-assembly ·
surface chemistry

Dedicated to Professor George R. Newkome on the occasion of his 70th birthday.

The local oxidation of self-assembled monolayers with a scanning probe is a promising method for the generation of structures with chemical functionalities on the nanometer scale. This technique, which takes advantage of the chemical stability and versatility of self-assembled monolayers and the ability to pattern these monolayers by scanning-probe-based oxidation methods, enables the hierarchical assembly of complex structures in a controlled manner. Surface modification can be followed by the assembly of a further functional monolayer and/or additional surface-modification reactions in the targeted, sequential construction of functional device features.

1. Introduction

The synthesis of nanometric functional components, such as nanoparticles and supramolecular assemblies, is a major driving force in nanotechnology.[1,2] However, the successful use of these materials with novel properties relies critically on their effective integration into frameworks of higher complexity. In nature, highly efficient structures with nanometer dimensions are all around us. The energy and resource efficiency of such systems has inspired researchers from the fields of chemistry, (micro)biology, physics, and engineering to develop complex synthetic devices with nanometer dimensions by hierarchical assembly based on the construction model observed in nature.

Two general methodologies are used for the assembly of functional nanostructures: The top-down approach builds on existing (optical) lithographic techniques to decrease the size of the components and thus increase their performance and value. Structures produced in this way are mainly of interest for their topographical features and may consist of different materials. However, the preparation of nanomaterials by this method has not yet been addressed sufficiently. In the bottom-up approach, small molecules are used as building blocks and assemble into larger, complex arrangements by supramolecular chemistry: through a combination of covalent and noncovalent interactions, including weak interactions, such as hydrogen-bonding, as well as ionic and metal–ligand interactions.[3,4]

Although both approaches have led to the construction of intricate structures with nanometer dimensions, a combination of both approaches is beneficial for certain applications, such as the development of sensors. The bottom-up approach is then used to introduce the necessary chemical or biological functionality, and top-down patterning methods are used to direct these functionalities to predefined positions on a suitable substrate. This combination of approaches, in which chemical functionalization plays an essential role, enables the comprehensive fabrication of tailor-made nanometric structures with high fidelity and reproducibility and offers several advantages to pure structuring approaches. The accessibility and flexibility made possible by the bottom-up fabrication steps are important for the assembly of complex devices, and specific binding sites based on chemical interactions can be generated. However, a method for the integration of chemical functionality into nanostructures must meet a series of requirements if the fabrication process is to be flexible

---

[*] Dr. D. Wouters, Dr. S. Hoeppener, Prof. Dr. U. S. Schubert
Laboratory of Macromolecular Chemistry and Nanoscience
Eindhoven University of Technology
5600 MB Eindhoven (The Netherlands)
Fax: (+31) 49-247-4186
E-mail: u.s.schubert@tue.nl
Dr. S. Hoeppener, Prof. Dr. U. S. Schubert
Center for Nanoscience (CeNS)
Ludwigs-Maximilians-Universität München
Amalienstrasse 54, 80799 (Germany)
Prof. Dr. U. S. Schubert
Laboratory of Organic and Macromolecular Chemistry
Friedrich-Schiller-Universität Jena
Humboldtstrasse 10, 07743 Jena (Germany)

enough to accommodate a wide range of structural features. Desired properties, such as stability, compatibility with chemical or biological functionalities, site specificity, high resolution, and versatility, have to be features of a competitive fabrication approach.

2. Recent Developments in Electrochemical Scanning-Probe Lithography

Scanning-probe-based lithography techniques fulfill many of the above-mentioned requirements. The ability to manipulate matter on the nanometer scale has attracted significant attention. The scanning probe microscope (SPM) can be used to create patterned structures with nanometer dimensions.[5–8] Dip-pen nanolithography,[9,10] in which thiolate monolayers are used to pattern substrates, is one of the most prominent methods for the selective functionalization of a substrate on the nanometer scale. The SPM can be used for both the local deposition of materials and the local removal or modification of materials. For example, in dynamic plow lithography,[11,12] the tip is pressed with high force onto a substrate, which leads to the formation of controlled indents or scratches on the surface. The resulting patterns, for example, in thin polymer layers on silicon, can be used subsequently in silicon-processing techniques. Similarly, a process known as nanoshaving can be used for the local removal of thiol molecules from a densely packed monolayer on gold.[13]

Kolb and Simeone[14] introduced an approach based on the "jump-to-contact" site-selective electrochemical deposition of metal clusters. In this method, the tip of a scanning tunneling microscope (STM) is kept at an electrode potential that is slightly more negative relative to the bulk deposition potential of metal ions in solution. As a result, the tip is reloaded continuously with metal ions. When the tip nears the surface, a metal bridge is formed between the tip and the substrate. Upon removal of the tip, the metal bridge is broken, and small clusters are formed on the substrate. This fast and reliable process was applied to a wide range of metal ions and substrates.

Daan Wouters studied chemical engineering at the Eindhoven University of Technology in the Netherlands. During this period he spent four months at DSM Desotech (Elgin, USA), where he carried out research on UV-curable coatings. After his graduation in 2000, he joined the Laboratory of Macromolecular Chemistry and Nanoscience headed by Prof. U. S. Schubert. After completing his PhD in 2005, he continued his research as a postdoctoral student in the same research group. He has been a project leader at the Holst Center in Eindhoven since 2008.

Stephanie Hoeppener studied physics at the University of Münster, Germany, where she completed her PhD in 2001 under the supervision of Prof. H. Fuchs and Prof. L. F. Chi with research on chemical surface templates and self-assembled monolayers. She then moved to the Weizmann Institute of Science, Israel, as a Minerva Fellow in the research group of Prof. J. Sagiv. In 2003, she joined the research group of Prof. U. S. Schubert at Eindhoven University of Technology in the Netherlands as project manager for nanolithography.

Ulrich S. Schubert completed his PhD in 1995 under the supervision of C. D. Eisenbach (Bayreuth, Germany) and G. R. Newkome (Florida, USA), carried out postdoctoral research with J.-M. Lehn at the Université de Strasbourg (France), and then moved to the Technische Universität München (Germany), where he completed his habilitation in 1999 (with O. Nuyken). He was appointed Full Professor at Eindhoven University of Technology (TU/e) in 2000 and returned to Germany in 2007 as Professor of Organic and Macromolecular Chemistry at the Friedrich-Schiller-Universität Jena. He remains professor part-time at TU/e.

The application of suitable bias voltages to the tip of a scanning force microscope (SFM) has been used for a number of different surface-patterning methods and extends the possibilities for the use of the SFM for nanofabrication. Approaches include the anodization of silicon, the voltage-induced local deposition of material onto surfaces, and the voltage-induced local desorption of material from surfaces. These approaches sometimes involve the use of self-assembled monolayers. Methods for the direct chemical functionalization of the monolayers include polymerization, end-group functionalization, and the cleavage of protecting groups on the monolayers. The local oxidation of silicon to silicon oxide[15] is compatible with conventional silicon-patterning technologies, as the resulting silicon oxide patterns can be transformed into three-dimensional surface structures in subsequent wet-etching steps.[16,17] Such structures, however, have no functional groups that can undergo interactions. The introduction of self-assembled monolayers is therefore regarded as a major development. Such monolayers have been used as resist materials[18,19] that can be patterned to control the formation of a stable water meniscus and thus increase the resolution of the oxidation process.[20,21]

In 1999, Sagiv and co-workers reported a new concept, whereby bias voltage pulses applied to a conductive SFM tip induce the electrochemical conversion of surface-exposed terminal groups of a self-assembled monolayer. In this way, chemical functionalities can be introduced directly onto a surface. The first report focused on the chemical patterning of nonadecyltrichlorosilane (NTS) monolayers with terminal vinyl groups on the surface;[22] however, the concept was later extended to the patterning of chemically inert *n*-octadecyltrichlorosilane (OTS) monolayers.[23] The resolution of this electrochemical oxidation process, which was also introduced as "constructive nanolithography", has been demonstrated to be lower than 10 nm.[23] The chemical oxidation of the top functional groups was confirmed by FTIR measurements performed on a macroscopic substrate that had been electro-oxidized with a copper grid. These measurements showed the presence of acid groups on the patterned monolayer and revealed that the monolayer was preserved during the electrooxidation process. Indirect evidence for the conversion of the methyl groups into acid functionalities (Figure 1 a) was provided by the observed reaction of the resulting monolayer with amines. Moreover, it was demonstrated that the substrates electrooxidised with a conductive TEM copper grid showed a reliable copy of the copper grid on their surface. Thus, the parallel patterning of large surface areas in one oxidation step is possible with this method.[24]

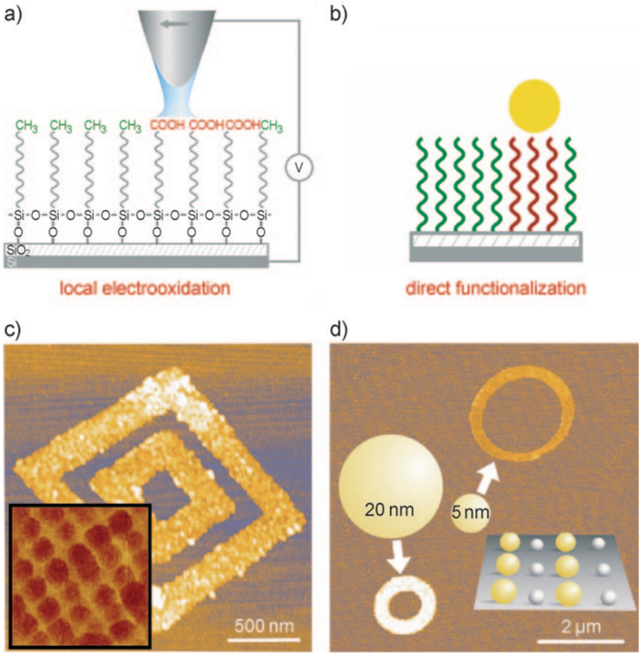

Figure 1. a) The local electrooxidation of *n*-octadecyltrichlorosilane monolayers induces the formation of carboxylic acid end groups, which can be used for b) the direct attachment of functional materials (yellow circle; red: COOH-functionalized monolayer; green: nonfunctionalized monolayer). Examples include c) magnetic iron nanoparticles generated in situ on the surface templates (SFM and magnetic force image of the particle array) and d) the assembly of different positively charged nanoparticles on the negatively charged carboxylic acid patterns. The background image shows an SFM image of the surface pattern generated in this way (reprinted with permission from the Royal Society of Chemistry). Both rings consist of gold nanoparticles with different sizes.

The possibilities for the chemical characterization of nanostructures are limited. To some extent, friction force imaging can provide indirect information on changes in the surface properties associated with the electrochemical oxidation.[23] In the case of OTS monolayers, which are strongly hydrophobic, electrochemical oxidation generates hydrophilic surface regions, as acid functionalities are formed. The adsorbed water layer in these regions causes increased frictional forces to operate on an SFM tip moved in contact mode across the structure. The resulting signal is a good indicator of a successful oxidation process. However, artifacts are frequently observed in the measurements as a result of the coupling of the topography signal with the frictional information.[25,26] This effect causes an apparent change in the topographic image in the electrooxidized areas of the monolayer. A reversal of the scan direction leads to an inversion of the contrast: a strong indication that the contrast observed in the topographic image is caused by the higher friction in these areas. This interpretation is also supported by modulated friction-force measurements,[26] which have confirmed that the topography of the patterned substrate remains featureless after the oxidative patterning, which indicates that the topographic artifacts are leveled out.

The parameters for the successful electrooxidation of OTS monolayers were determined on the basis of these findings.[26] Figure 2 a shows the dependence of the oxidation time on the applied voltage. The electrooxidation of the monolayer (and thus the formation of acid groups) proceeds under a relatively narrow range of oxidation conditions (middle area of picture). Outside this small window, either no modification takes place (right side of picture), or the monolayers are degraded and the growth of silicon oxide dominates the modification process (left side of picture).

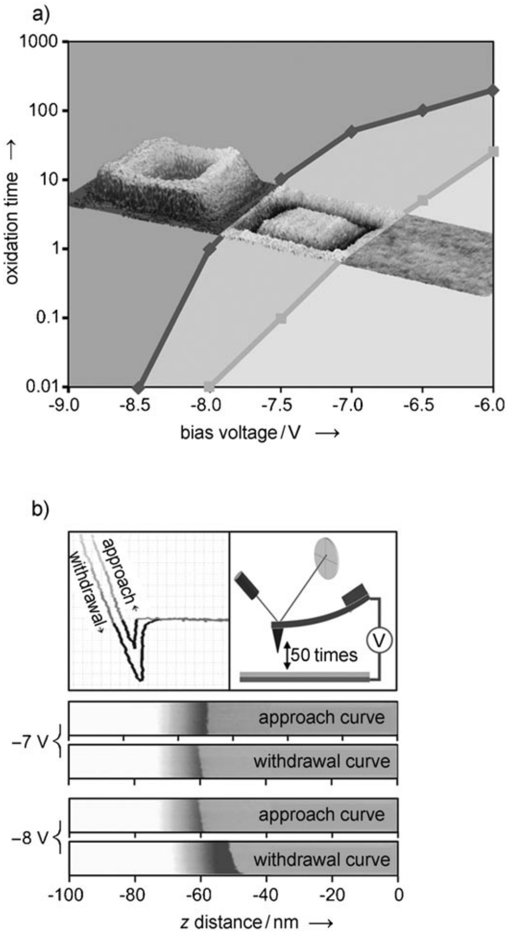

Figure 2. a) The local electrooxidation of *n*-octadecyltrichlorosilane monolayers results in the formation of carboxylic acid groups only within a small window in terms of the bias voltage and pulse duration (middle area of the diagram). b) SFM force spectroscopy may be used to evaluate the oxidation process. The oxidation process can also be monitored by force–distance curves recorded with a biased tip. The snap-in and snap-out points of the force–distance curves shift as the oxidation progresses as a result of the changes in the surface properties.

Additional parameters that influence the patterning process are the applied bias voltage, the humidity, and the tip material. The strong dependence of the oxidation process on the formation of a stable water meniscus was recognized in early studies: Control experiments in dry air did not result in any pattern formation.[22] The importance of the water meniscus was confirmed further by the use of a flat stamp with hydrophilic and hydrophobic areas on the surface for the electrochemical oxidation of the monolayer. These stamps may be produced by electrooxidative patterning or other techniques. The successful direct transfer of a pattern from hydrophilic electrooxidized surface areas to an OTS monolayer in a further electrooxidation step[27] indicates the important role of water menisci in the induction of the electrochemical oxidation process.

Moreover, the change in the surface properties of the monolayer during the oxidation process enabled the in situ investigation of the oxidation process. Force-versus-distance curves were recorded continuously while the voltage required for the oxidation was applied to the tip (Figure 2 b).[28] In this way, changes in the wetting properties of the modified area could be probed during the oxidation process. Changes in adhesion during the oxidation were analyzed, and a fast transition from monolayer oxidation to the degeneration of the monolayer and subsequent growth of silicon dioxide was observed.

Pignataro et al. used time-of-flight secondary ion mass spectrometry (TOF-SIMS) to analyze in detail the oxidation process that occurred on self-assembled monolayers formed on hydrogenated substrates.[29] They observed the formation of a friction contrast for both positive and negative voltages, whereby the application of negative tip bias voltages resulted in a more pronounced modification of the monolayer. TOF-SIMS investigations also revealed the presence of C_xH_yO and C_xH_yN species in the modified regions. These species were thought to derive from polar organic moieties formed during the electrochemical oxidation process; in particular, the formation of CHO groups was suggested. Reactive oxygen-rich radicals formed at the interface between the tip and the self-assembled monolayer are thought to play an important role in the reaction. Moreover, evidence was found for the involvement of activated carbon moieties and nitrogen-containing species in the reaction environment. However, so far, it has not been possible to determine the exact oxidation mechanism.

3. Chemically Active Surface Templates for Functionalization Processes

Electrooxidative lithography is a versatile technique for the fabrication of chemically structured surfaces on the nanometer and micrometer scales for potential use in further derivatization steps. The local generation of polar surface groups is of great interest, as they can be transformed directly in chemical reactions or used for the local attachment and stabilization of a variety of nanomaterials on the inscribed surface. In this way, the patterned surfaces can be used as templates for the fabrication of (functional) nanostructures. A variety of interactions can be used to attach the nano-objects, including covalent, electrostatic, and hydrogen-bonding interactions, as well as complexation.

The structures can be functionalized by the direct assembly of the material onto the patterns, the assembly of multilayers, or end-group-modification reactions.[23,30] Templates can be used to study the wetting behavior of alcohols on nanopatterned lines[31] or for the wetting-driven assembly of metal ions on the substrate.[32] Figure 1 summarizes two modification approaches that illustrate the potential of electrooxidative lithography for the creation of templates for the guided assembly of nanoparticles. Figure 1 c shows an example of the in situ generation of magnetic nanoparticles on a surface template, whereby individual iron nanoparticles were synthesized on template structures in a two-step process: Iron ions were adsorbed onto a hydrophilic template from an aqueous solution of iron(II) acetate and then reduced to iron(0) with hydrazine vapor.[33] The magnetic properties of the resulting particles were investigated with magnetic force microscopy; measurements with and without an external magnetic field demonstrated that the particles were superparamagnetic.

Positively charged ready-formed nanoparticles can also be assembled on acid-functionalized surface templates. In this case, the electrostatic interaction between the template and the nanoparticles is the binding force for the selective attachment of the nanoparticles. The particles organize themselves onto the surface template with a high fidelity. Other examples of this type of functionalization include the guided self-assembly of iron nanoparticles,[25] CdSe/ZnS core/shell nanoparticles,[34] and gold nanoparticles.[35] Multicomponent assemblies, formed for instance by the assembly of gold nanoparticles of different sizes, can be created by sequential oxidation and functionalization steps (Figure 1 d).[36] This method is an important step towards the fabrication of, for example, nanoelectronic device features, as it offers the unique possibility of combining different materials within a framework of higher complexity.

The versatility of the surface templates can be enhanced tremendously by the site-selective assembly of molecular building blocks to provide tailor-made binding groups. In this approach, carboxylic acid groups on the template are used for the assembly of molecular layers. In particular, silane molecules play an important role, as they form stable overlayers on the template structures.[23] For example, overlayers of vinyl-substituted NTS can be used to generate amine and thiol functionalities by photochemical reactions of the vinyl groups. These functional groups can be utilized in subsequent self-assembly steps to bind, for example, Au_{55} nanoclusters[37] or gold colloids (Figure 3 b).[38] A similar strategy was employed to generate conductive nanowire structures on a thiol-functionalized bilayer.[30] Commercially available silanes can also be used to introduce chemical functionality. 3-Aminopropyltrimethoxysilane (APTMS) is a versatile molecule that has been used in a number of surface-modification approaches.[39] For example, it can be used for the local assembly of negatively charged nanoparticles. Although commercially available silanes offer a variety of possibilities for the stabilization of different materials, they do

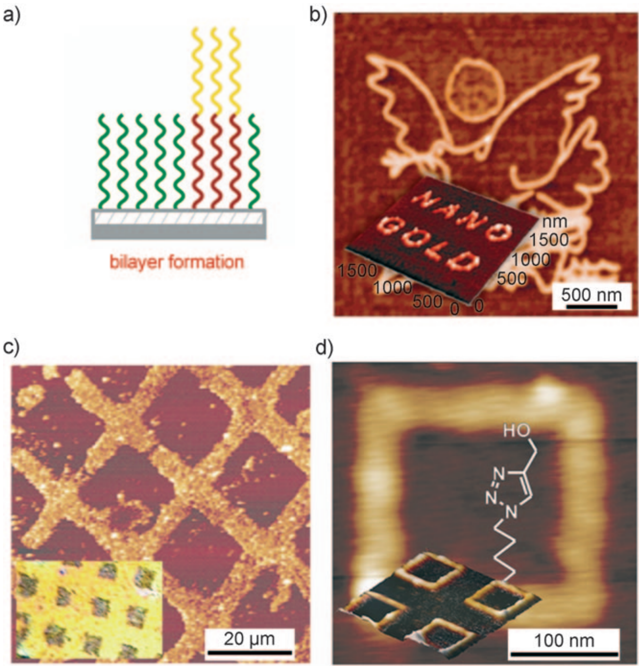

Figure 3. a) Chemical surface patterning can be used for the site-selective assembly of additional silane monolayers. b) This process enables the introduction of a variety of functional groups, which can be used to promote the self-assembly of negatively charged nanoparticles, such as Au55 nanoclusters on the inscribed patterns. c) The self-assembly of 11-bromoundecyltrichlorosilane as a second layer on top of an inscribed pattern enables the use of these structures as initiators for ATRP polymer grafting. The tapping mode SFM image shows polystyrene brushes grafted from the oxidized areas. d) Such templates can also be modified by using "click chemistry", for example, the local binding of propargyl alcohol to azide groups on the surface. The SFM image represents an inscribed structure modified with propargyl alcohol.

not form well-defined, ordered overlayers. 11-Bromoundecyltrichlorosilane can be used to initiate controlled atom transfer radical polymerization (ATRP), which begins on the surface template and proceeds with the formation of patterned polymer brushes and even block copolymers (Figure 3c).[40] Furthermore, bromine-terminated overlayers can be converted into azide-functionalized structures, which can be used subsequently as templates for cycloaddition reactions with alkynes (Figure 3d).[41] By this method, also known as "click" chemistry,[42] a broad variety of functional groups[43,44] or functional molecules, such as dyes,[45] may be assembled onto the substrate. The formation of molecular overlayer structures offers numerous possibilities for the tailoring of surface properties and the introduction of selectivity and addressability in the lithographic approach to the assembly of functional nanostructures.

Basnar et al. used tyramine as a precursor molecule to generate catechol entities on surface structures through a tyrosinase-catalyzed oxidation reaction. The catechol entities were used to bind boronic acid functionalized gold and magnetic particles.[46] Cai and Ocko combined the electrooxidation with dip-pen nanolithography by carrying out the oxidation with a tip that was loaded with molecules (the "ink"). They suggested the use of two distinct inks: quaternary ammonium salts and 3-mercaptopropyltrimethoxysilane (MPTMS). Upon oxidation of the OTS monolayer, these molecules were transferred onto the surface, as indicated by an increase in height in tapping-mode SFM images. This technique enables the direct deposition of molecular overlayers during the electrooxidation.[47] With MTPMS overlayers, the adsorption of Au nanoparticles was demonstrated.

4. Alternative Methods for the Functionalization of Surfaces

Other examples of the electrochemical modification of substrates with the aim of creating chemically modified surface areas include the use of alternative monolayers, such as amine monolayers protected with α,α-dimethyl-3,5-dimethoxybenzyloxycarbonyl (DDZ) groups.[48] Fresco and Fréchet postulated that the ionic reaction to cleave the DDZ groups occurred by heterolytic bond cleavage followed by elimination of the carbocation. During the course of the reaction promoted by the intense local electric field produced by the SFM tip, 3,5-dimethoxy-α-methylstyrene, carbon dioxide, and a primary amine were formed. The local assembly of dendritic macromolecules served as indirect evidence for the successful cleavage of the protecting group. Other protected silane monolayers were also used. The local oxidation of these monolayers cleaved the protecting group to reveal a buried thiol functionality.[49] The thiol groups were used in the subsequent assembly of gold nanoparticles (Figure 4).

Alternatively, polymeric films can be used for the local modification of the chemical structure of a substrate. Chang et al. used metallic masks biased with a suitable voltage to modify the properties of a thin layer of poly(*N*-Boc-2-aminoethyl methacrylate) on a conductive gold-coated substrate (Boc = *tert*-butoxycarbonyl).[50] During the electrolithographic process, acids were generated within the polymer layer. In an additional annealing step, the acids facilitated the dissociation of the Boc groups from the amine functional groups to generate an amino-terminated surface area. These templates were used to bind a fluorescent biotin–streptavidin complex selectively. A resolution of about 300 nm is possible with this method. To prevent undesired coupling reactions in subsequent modification steps, protection of the initial amine functionalities with Boc groups over the whole surface of the resist is essential, as the process relies on a local electro-induced deprotection of the amine groups. Jegadesan et al. applied an electrically biased SFM tip for the local formation of conducting nanostructures of polycarbazoles through the direct electrochemical polymerization of thin films of poly(vinylcarbazole) and carbazole monomer (Figure 5).[51] The direct fabrication of conductive structures under ambient conditions on the spin-coated films was thus demonstrated.

Jang et al. extended this approach to insulating substrates by using a solid-state oxidative cross-linking process to produce conductive polymer structures locally.[52,53] Thus, a layer of insulating precursor molecules in the swollen state was brought into contact with an SFM tip that was biased with a potential sufficient to initiate the cross-linking of the

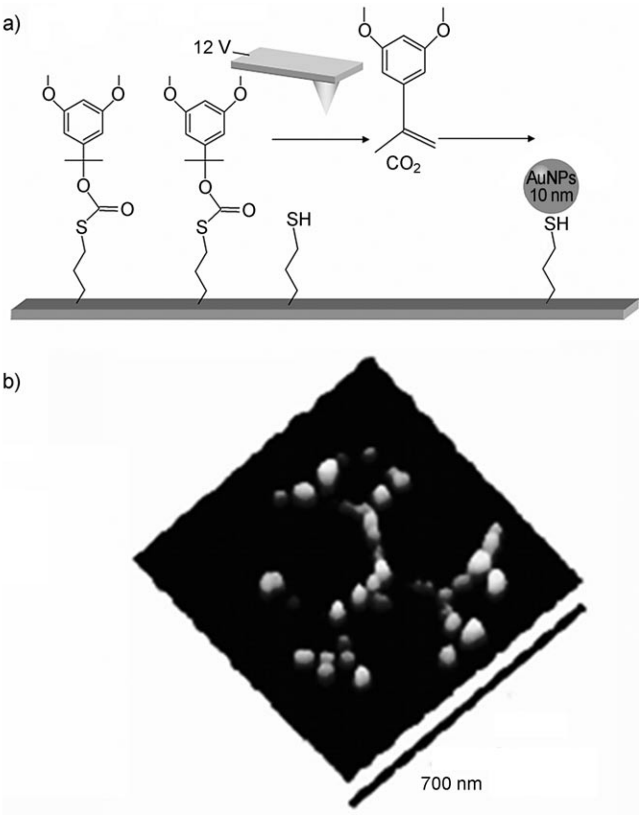

Figure 4. a) Cleavage of a DDZ-protected monolayer. Deprotection by electrooxidative lithography leads to thiol-functionalized surface patterns that can be used, for example, for the self-assembly of gold nanoparticles (NPs) of 10 nm diameter. b) SFM image of gold nanoparticles self-assembled on a deprotected surface (reprinted with permission from the American Chemical Society).

molecules to form a conductive polymer film. This process, which proceeds with almost complete conversion, does not depend on the substrate. It thus enables the straightforward and efficient formation of conducting features on surfaces.

Chemical modifications can not only be made by applying electrical bias pulses, but also by catalytic and photochemical approaches. For example, near-field scanning optical microscopy (NSOM) can be used for the lithographic step.[54] Leggett and co-workers developed a near-field optical photolithography approach in which UV light is used for the local oxidation of self-assembled monolayers on gold. In this process, thiols on the monolayer are oxidized to thiolates, which desorb from the surface and may be replaced by other molecules (Figure 6a).[55,56] The method is based on an NSOM setup with a UV laser. The resulting patterns may have a resolution of below 100 nm. Further studies by the same research group on monolayers on silicon with chloromethylphenyl entities revealed that these entities can be converted into aldehydes and/or acid groups under UV irradiation. The chemical composition of the modified surface areas depends on the dose of UV irradiation. Various monolayers were used in combination with this patterning method to generate active nanostructures. For example, the fabrication of biologically active nanostructures on chloromethylphenylsiloxane monolayers was demonstrated, for example, for DNA assembly (Figure 6b).[57]

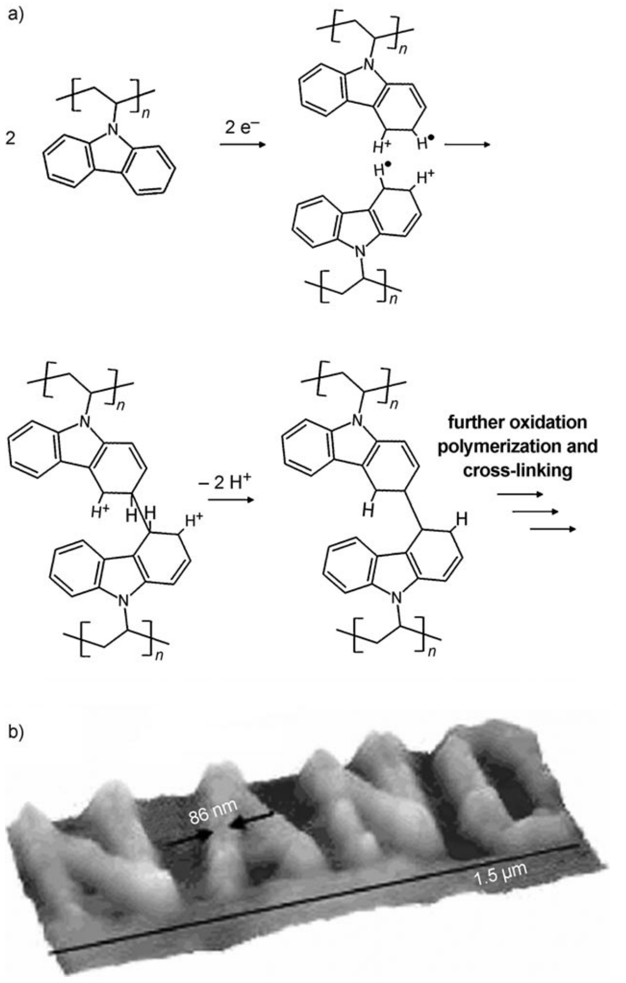

Figure 5. Tip-induced formation of conductive nanostructures on spin-coated films of carbazoles. a) Polymerization and cross-linking process. b) SFM topography image of a polymerized carbazole monomer film (reprinted with permission from the American Chemical Society).

A similar patterning method, in which electron-beam irradiation is used instead of a UV laser, was introduced by Goelzhäuser and co-workers, who used aromatic self-assembled layers as templates for the local generation of amino-functionalized surface structures (Figure 6c). These structures served as versatile templates for the local binding of fluorescently labeled proteins.[58] In this method, the electron beam transforms the terminal nitro functionalities of monolayers of 4′-nitro-1,1′-biphenyl-4-thiol into amino groups. The underlying aromatic layer is cross-linked simultaneously through dehydrogenation. Under conditions of low-energy electron proximity printing with a conventional electron beam, amine-functionalized structures with a lateral resolution of approximately 20 nm could be fabricated. These templates were used for the surface immobilization of fluorinated carboxylic acid anhydrides and rhodamine dyes,[59] and for the surface-initiated radical polymerization of polystyrene brushes.[60] Such cross-linking can also be applied for the site-selective deposition of metals, as the

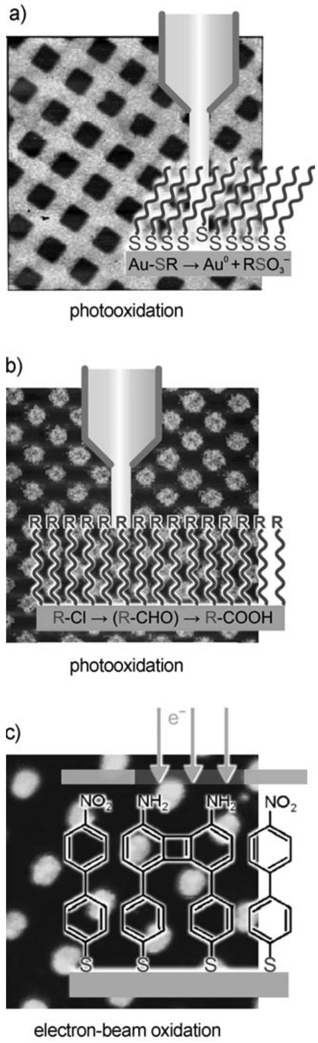

Figure 6. Electrooxidation with a UV beam can cause a) the local desorption of monolayers from gold substrates. The SFM image represents the topography of a patterned monolayer (reprinted with permission from the American Chemical Society) and b) end-group transformation through photooxidation on silicon. The patterns can be used for the site-selective assembly of aminefunctionalized nanoparticles, as can be seen in the corresponding SFM image (reprinted with permission from the American Chemical Society). c) Self-assembled monolayers can also be oxidized with an electron beam. SFM image of the patterned structure (reprinted with permission from Elsevier).

electron-induced changes have a distinct influence on the electrochemical properties of the monolayer. The process is only selective within a relatively narrow potential range, which depends on the monolayer type and the electrolyte. Following optimization of the deposition parameters, a resolution of approximately 30 nm for single lines and 50 nm for line gratings was observed for Cu and Co deposition.[61]

5. Conclusions and Outlook

The examples presented herein demonstrate the power of employing chemically active surface structures for nanofabrication. These structures have an extraordinary ability to stabilize nanomaterials introduced by classical self-assembly schemes. The cost-effectiveness of this fabrication process is an important advantage if it is to be integrated into device production.

Even though electrooxidative lithography provides a wide range of useful possibilities for the manipulation of materials on the nanometer scale and is highly competitive with alternative approaches, its further development is essential. Not only is the development of new procedures in surface chemistry to enable the synthesis of a broad range of surfaces with a variety of chemically useful functional groups of fundamental importance, but the use of alternative substrates will also be crucial, for example, for the structuring of biological material. Primary results demonstrate the feasibility of patterning monolayers that are assembled on transparent, ultrasmooth indium tin oxide films. This approach opens the possibility of combining structuring techniques with (near-field) optical methods. Moreover, it would be desirable to develop strategies for the structuring of large surface areas with nanometer-scale templates, for example, for investigations into the adhesion properties of cells and tissues.

Further investigation of the oxidation process and subsequent functionalization steps is important for the tailored fabrication of patterned structures. New high-resolution characterization tools are required for nanometric structures, as current techniques, such as FTIR and X-ray photoelectron spectroscopy, require larger patterned areas owing to their limited resolution and the small amount of material present in a monolayer system.

The preparation of large nanostructured surface areas is also possible through a recently reported automated patterning approach.[62] This approach can be improved further by using a multiple-tip array. In this feasibility study, large surface areas were patterned with a system composed of four SFM tips operating simultaneously. Additional possibilities have evolved from the electrooxidative printing approach, the lateral resolution of which must be improved. Furthermore, approaches for three-dimensional patterning should be investigated in more detail.

Besides the local end-group modification of self-assembled monolayers, the use of monolayers containing electrochemically cleavable functional groups should be possible. Although the introduction of latent chemical functionality in the nonpatterned region would broaden the chemical versatility of the electrooxidation method significantly, such techniques require additional synthetic effort, and the self-assembly of these materials may not lead to the formation of densely packed, highly ordered monolayers. Acid-generating resist layers that can be used on a multitude of different substrates may provide an alternative; however, subsequent surface-modification steps are limited owing to the possibility of undesired reactions with the substrate.

The combination of different patterning techniques may offer solutions to problems in nanofabrication, for example, the fabrication of nanoelectronic circuits. However, these techniques have to be optimized, in particular with respect to their compatibility with other processes. The introduction of orthogonal binding schemes might help to overcome these difficulties. Critical issues with respect to functional nanostructures are their applicability, the time and expense associated with their fabrication, and their suitability for mass production. Many of the techniques described herein still have deficiencies in these areas.

We thank the Nederlandse Wetenschappelijk Organisatie (NWO, VICI award for U.S.S.) for financial support.

Received: March 2, 2008

[1] G. Hodes, *Adv. Mater.* **2007**, *19*, 639 – 655.
[2] V. Palermo, P. Samori, *Angew. Chem.* **2007**, *119*, 4510 – 4514; *Angew. Chem. Int. Ed.* **2007**, *46*, 4428 – 4432.
[3] J.-M. Lehn, *Chem. Soc. Rev.* **2007**, *36*, 151 – 160, and references therein.
[4] J.-M. Lehn, *Supramolecular Chemistry*, Wiley-VCH, Weinheim, **1995**.
[5] D. Wouters, U. S. Schubert, *Angew. Chem.* **2004**, *116*, 2534 – 2550; *Angew. Chem. Int. Ed.* **2004**, *43*, 2480 – 2495.
[6] S. Krämer, R. R. Fuierer, C. B. Gorman, *Chem. Rev.* **2003**, *103*, 4367 – 4418.
[7] M. Geissler, Y. Xia, *Adv. Mater.* **2004**, *16*, 1249 – 1269.
[8] A. A. Tseng, A. Notargiacomo, T. P. Chen, *J. Vac. Sci. Technol. B* **2005**, *23*, 877 – 894.
[9] M. Jaschke, H.-J. Butt, *Langmuir* **1995**, *11*, 1061 – 1064.
[10] D. S. Ginger, H. Zhang, C. A. Mirkin, *Angew. Chem.* **2004**, *116*, 30 – 46; *Angew. Chem. Int. Ed.* **2004**, *43*, 30 – 45.
[11] T. A. Jung, A. Moser, H. J. Hug, D. Brodbeck, R. Hofer, H. R. Hidber, U. D. Schwarz, *Ultramicroscopy* **1992**, *42–44*, 1446 – 1251.
[12] M. Heyde, K. Rademann, B. Cappella, M. Geuss, H. Sturm, T. Spangenberg, H. Niehus, *Rev. Sci. Instrum.* **2001**, *72*, 136 – 141.
[13] J.-F. Liu, S. Cruchon-Dupeyrat, J. C. Garno, J. Frommer, G.-Y. Liu, *Nano Lett.* **2002**, *2*, 937 – 940.
[14] D. M. Kolb, F. C. Simeone, *Electrochim. Acta* **2005**, *50*, 2989 – 2996.
[15] J. Dagata, J. Schneir, H. H. Harary, C. J. Evans, M. T. Postek, J. Bennett, *Appl. Phys. Lett.* **1990**, *56*, 2001 – 2003.
[16] D. A. Weinberger, S. Hong, C. A. Mirkin, B. W. Wessels, T. B. Higgins, *Adv. Mater.* **2000**, *12*, 1600 – 1603.
[17] S. Sun, K. S. L. Chong, G. J. Leggett, *Nanotechnology* **2005**, *16*, 1798 – 1808.
[18] J. Zheng, Z. Zhu, H. Chen, Z. F. Liu, *Langmuir* **2000**, *16*, 4409 – 4412.
[19] M. Shin, M.-C. Kwon, S. K. Kim, H. J. Kim, Y. Roh, B. Hong, J. B. Park, H. Lee, *Nano Lett.* **2006**, *6*, 1334 – 1338.
[20] J. Park, H. Lee, *Mater. Sci. Eng. C* **2004**, *24*, 311 – 331.
[21] B. Kim, H. Park, S.-H. Lee, W. M. Sigmund, *Colloid. Surf. A* **2005**, *253*, 23 – 26.
[22] R. Maoz, S. R. Cohen, J. Sagiv, *Adv. Mater.* **1999**, *11*, 55 – 61.
[23] R. Maoz, E. Frydman, S. R. Cohen, J. Sagiv, *Adv. Mater.* **2000**, *12*, 725 – 731.
[24] S. Hoeppener, R. Maoz, J. Sagiv, *Nano Lett.* **2003**, *3*, 761 – 767.
[25] S. Hoeppener, A. S. Susha, A. L. Rogach, J. Feldmann, U. S. Schubert, *Curr. Nanosci.* **2006**, *2*, 135 – 141.
[26] D. Wouters, R. Willems, S. Hoeppener, C. F. J. Flipse, U. S. Schubert, *Adv. Funct. Mater.* **2005**, *15*, 938 – 944.
[27] S. Hoeppener, R. Maoz, J. Sagiv, *Adv. Mater.* **2006**, *18*, 1286 – 1290.
[28] S. Hoeppener, J. H. K. van Schaik, U. S. Schubert, *Adv. Funct. Mater.* **2006**, *16*, 76 – 82.
[29] B. Pignataro, A. Licciardello, S. Cataldo, G. Marletta, *Mater. Sci. Eng. C* **2003**, *23*, 7 – 12.
[30] S. Hoeppener, R. Maoz, S. R. Cohen, L. F. Chi, H. Fuchs, J. Sagiv, *Adv. Mater.* **2002**, *14*, 1036 – 1041.
[31] A. Checco, O. Gang, B. M. Ocko, *Phys. Rev. Lett.* **2006**, *96*, 056104; O. Gang, K. J. Alvine, M. Fukuto, P. S. Pershan, C. T. Black, B. M. Ocko, *Phys. Rev. Lett.* **2006**, *97*, 039902 (Erratum: CA144:136131).
[32] D. Chowdhury, R. Maoz, J. Sagiv, *Nano Lett.* **2007**, *7*, 1770 – 1778.
[33] S. Hoeppener, U. S. Schubert, *Small* **2005**, *1*, 628 – 632.
[34] D. Wouters, S. Hoeppener, U. S. Schubert, *Proceedings ICN + T* 2006 Basel, ISBN 3-905084-71-6, p. 186.
[35] D. Wouters, U. S. Schubert, *Langmuir* **2003**, *19*, 9033 – 9038.
[36] D. Wouters, U. S. Schubert, *J. Mater. Chem.* **2005**, *15*, 2353 – 2355.
[37] S. Liu, R. Maoz, G. Schmid, J. Sagiv, *Nano Lett.* **2002**, *2*, 1055 – 1060.
[38] S. Liu, R. Maoz, J. Sagiv, *Nano Lett.* **2004**, *4*, 845 – 851.
[39] T. Strother, R. J. Hamers, L. M. Smith, *Nucleic Acids Res.* **2000**, *28*, 3535 – 3541.
[40] C. R. Becer, C. Haensch, S. Hoeppener, U. S. Schubert, *Small* **2007**, *3*, 220 – 225.
[41] R. Huisgen in 1, 3-Dipolar Cycloaddition Chemistry (Ed.: A. Padwa), Wiley, New York, **1984**, pp. 1–176.
[42] H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem.* **2001**, *113*, 2056 – 2075; *Angew. Chem. Int. Ed.* **2001**, *40*, 2004 – 2021.
[43] For a recent review, see: H. Nandivada, X. Jiang, J. Lahann, *Adv. Mater.* **2007**, *19*, 2197 – 2208.
[44] For a recent review, see: J.-F. Lutz, *Angew. Chem.* **2007**, *119*, 1036 – 1043; *Angew. Chem. Int. Ed.* **2007**, *46*, 1018 – 1025.
[45] C. Haensch, S. Hoeppener, U. S. Schubert, *Nanotechnology* **2008**, *19*, 035703.
[46] B. Basnar, J. Xu, I. Willner, *Langmuir* **2007**, *23*, 2293 – 2296.
[47] Y. Cai, B. M. Ocko, *J. Am. Chem. Soc.* **2005**, *127*, 7408 – 7412.
[48] Z. M. Fresco, I. Suez, S. A. Backer, J. M. Fréchet, *J. Am. Chem. Soc.* **2004**, *126*, 8374 – 8375.
[49] Z. M. Fresco, J. M. Fréchet, *J. Am. Chem. Soc.* **2005**, *127*, 8302 – 8303.
[50] Y. Chang, Y. S. Ahn, H. T. Hahn, Y. Chen, *Langmuir* **2007**, *23*, 4112 – 4114.
[51] S. Jegadesan, S. Sindhu, R. C. Advincula, S. Valiyaveettil, *Langmuir* **2006**, *22*, 780 – 786.
[52] S. Y. Jang, M. Marquez, G. A. Sotzing, *J. Am. Chem. Soc.* **2004**, *126*, 9476 – 9477.
[53] S. Y. Jang, M. Marquez, G. A. Sotzing, *Synth. Met.* **2005**, *152*, 345 – 348.
[54] E. Betzig, J. K. Trautman, R. Wolfe, E. M. Gyorgy, P. L. Finn, M. H. Kryder, C.-H. Chang, *Appl. Phys. Lett.* **1992**, *61*, 142 – 144.
[55] K. S. L. Chong, S. Sun, G. J. Leggett, *Langmuir* **2005**, *21*, 3903 – 3909.
[56] S. Sun, G. J. Leggett, *Nano Lett.* **2002**, *2*, 1223 – 1227.
[57] S. Sun, M. Montague, K. Critchley, M.-S. Chen, W. J. Dressick, S. D. Evans, G. J. Leggett, *Nano Lett.* **2006**, *6*, 29 – 33.
[58] A. Biebricher, A. Paul, P. Tinnefeld, A. Goelzhäuser, M. J. Sauer, *J. Biotechnol.* **2004**, *112*, 97 – 107.
[59] W. Geyer, V. Stadler, W. Eck, A. Goelzhäuser, M. Grunze, M. Sauer, T. Weimann, P. Hinze, *J. Vac. Sci. Technol. B* **2001**, *19*, 2732 – 2735.
[60] U. Schmelmer, R. Jordan, W. Geyer, W. Eck, A. Goelzhaeuser, M. Grunze, A. Ulman, *Angew. Chem.* **2003**, *115*, 577 – 581; *Angew. Chem. Int. Ed.* **2003**, *42*, 559 – 563.
[61] B. Voelkel, G. Kaltenpoth, M. Handrea, M. Sahre, C. T. Nottbohm, A. Kueller, A. Paul, W. Kautek, W. Eck, A. Goelzhäuser, *Surf. Sci.* **2005**, *597*, 32 – 41.
[62] D. Wouters, U. S. Schubert, *Nanotechnology* **2007**, *18*, 485306.