Combination of self-assembly and nanolithography as an effective nanofabrication methodology for device realization

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Scanning probe-based nanolithography techniques are advantageous and have the potential to replace the expensive photolithography process. One of the scanning probe techniques is constructive nanolithography, which is a nano-electrochemical process of oxidizing only the terminal $-CH_3$ group to $-COOH$ of the highly ordered monolayer of OTS (n-octadecyltrichlorosilane) self-assembled on silicon with a conducting scanning force microscope tip. Making use of surface self-assembly in combination with constructive nanolithography various species such as metals, metal ions, semiconductor nanoparticles and organic compounds can be assembled, over which reactions and reorganization processes can take place for their further use as nanodevices.

Keywords: Atomic force microscope, nanodevice, nanolithography, nanoreactors, self-assembled monolayer.

ONE of the areas nanotechnology has excelled is in miniaturization of devices. The interest in miniaturization is driven by the advantages such devices possess in terms of greater efficiency and sensitivity, lower power consumption and better device integration. Lithography using light, i.e. photolithography is one of the most successful techniques and has served the microelectronics industry for a long time. The resolution (R) of the features that can be achieved using light of wavelength (λ) is given by the relation $R = k_1\lambda/NA$, where k_1 is a constant, and NA the numerical aperture. To reduce the resolution of the features, either λ or k_1 has to be reduced or NA has to be increased. This has led to the use of X-ray, ions and electrons as in X-ray lithography, ion-beam lithography and electron beam lithography respectively, to make smaller features. All these above-mentioned techniques, which are just a modification of photolithography, have led to the development of features below 100 nm. But in all these techniques owing to the problem of optical diffraction, feature size is limited by the wavelength of the exposing radiation used for photochemical transformations. As the demand

for making nanofeatures continues as a result of added advantages, the need arises to overcome the fundamental intrinsic resolution problem. There are other techniques which have come up as a viable alternative to photolithography such as stamping or moulding methods, i.e. soft lithography[1-3], nanoimprint lithography[4-6], nanosphere lithography/colloidal lithography[7-9] and scanning probe microscopy-based techniques[10,11].

Development of patterning technique is governed by the fact that it will help make templates for assembling materials, which is the first requirement for device fabrication. Such an assembly of molecules/materials is called directed self-assembly, which involves the utilization of structure-directing additives, often organic molecules, and thus in principle different from spontaneous self-assembly. Template-guided self-assembly may involve the use of lithography or patterned surface fabricated by other processes. The ideal situation will be selective, periodic assembling of materials. Making an assembly of various smart materials like metal nanoparticles is important owing to the large number of applications it has as photonic materials[12-15], high-density magnetic data-storage devices[16], microchip reactors[17] and biosensors[18-21]. The property of self-organizing referred to as self-assembly of organic molecules, can be utilized for this purpose; the term 'self-assembling' monolayer was coined by an anonymous writer (see New Scientist, 1983, 98, 20) with reference to a paper by Netzer and Sagiv[22]. The organic self-assembled monolayer (SAM) has the potential of probing its use as a device. The advantage with SAM is that it can be controlled at the molecular level by altering the head group, tail group or backbone composition, making it chemically diverse. Moreover, densely packed SAM of any functional group can be made. The most conventional method of having SAM on silicon has relied on siloxane chemistry, where the organic molecule is attached to the substrate through Si–O–Si bonds.

The driving forces operating for molecular self-organization can be ionic, covalent, hydrogen and non-covalent, resulting in properties not found in individual components. The material self-assembly can cover all scales and the forces responsible for self-assembly beyond

molecular are capillary, colloidal, elastic, electric and magnetic. The advantage of such systems is that it proceeds towards the state of lower free energy and greater structural stability. There has been continuous development in the recent past to make assemblies of different materials on a variety of surfaces. The study in this direction will help in the realization of devices and/or circuits with functionalities comparable to conventional integrated circuits. Various scanning probe lithography (SPL) techniques are discussed here. The SPL techniques discussed here are not exhaustive; only a few of them have been listed. The article also discusses in detail one of the SPL methods, i.e. constructive nanolithography, and how its combination with self-assembly can be effectively utilized to generate hierarchical structures leading to various 2D and 3D structures.

Scanning probe lithography techniques

Among all the techniques, SPL is highly promising for nanofabrication at the nanometre scale. In this nanolithography technique, writing is carried out using sharp probe tips with the atomic force microscope (AFM). The advantages of SPL are that first, nanolithography can be carried out under ambient conditions and does not require state-of-the-art and sophisticated machinery. Secondly, with the availability of sharper AFM tips fabrication with feature sizes below 10 nm level is possible. There are several SPL techniques developed, namely dip-pen AFM lithography, local anodic oxidation, mechanical plowing and constructive nanolithography.

Dip-pen lithography

Mirkin and co-workers have pioneered the dip-pen lithography technique (DPN), in which the material is transferred from AFM tip to the surface. Material on the AFM tip acts as ink and is transferred to the substrate by capillary forces (Figure 1). Using DPN, a wide range of mate-
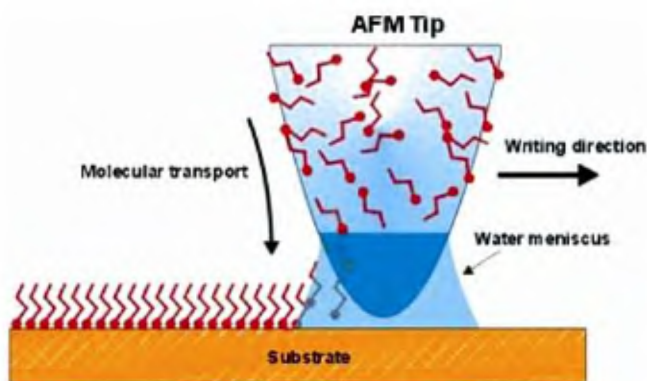
Figure 1. Scheme showing dip-pen nanolithography (courtesy: C. A. Mirkin and his group).

rials have been assembled on different substrates. Mirkin and co-workers have used DPN to deposit nanoarrays of proteins, IgG and lysozome on gold substrate[11]. An organic molecule like hexamethyldisilazane (HMDS) can be used as ink in DPN to deposit monolayers of HMDS on silicon and gallium arsenide surfaces[23].
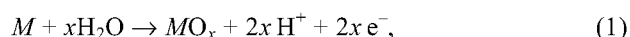
Ding et al.[24] deposited nanoscaled structures of semiconducting CdS materials using DPN. DPN-based generation of nanometre-scale magnetic structures with precise feature size control was also successfully demonstrated. Magnetic iron-oxide nanoparticles were prepared by the slow addition of an aqueous solution of ferrous chloride to an aqueous solution of ferric chloride at room temperature. The 16-mercaptohexadecanoic acid (MHDA) templates were used to assemble the magnetic nanostructures[25]. DPN was also successfully utilized to assemble collagen and a collagen-like peptide down to 30–50 nm line widths[26], as well as in the patterning of oligonucleotides[27]. Patterning of oligonucleotides was achieved by covalently anchoring the nanoscale patterns of oligonucleotides on both metallic and insulating substrates. Modification of DNA with hexanethiol groups allowed patterning on gold and oligonucleotides bearing the 5'-terminal acrylamide groups could be patterned on derivatized silica resulting in sequence-specific binding properties of the DNA from which they were composed. Mirkin and co-workers have shown that DPN can be used for the direct patterning of organic/inorganic composite nanostructures on silicon and oxidized silicon substrates. The approach works by the hydrolysis of metal precursors in the meniscus between an AFM tip and a surface according to the reaction $2M \, Cl_n + nH_2O \rightarrow M_2O_n + 2n \, HCl$, where $M = Al$, Si and Sn. The inks in this case are hybrid composites of inorganic salts with amphiphilic block copolymer surfactants. Using this concept Al_2O_3, SiO_2 and SnO_2 nanostructures on silicon and silicon oxide surfaces were fabricated[28]. Patterns of alkoxysilane which are difficult to generate by DPN can be obtained by controlling the degree of polymerization through careful choice of the alkoxysilane used as the 'ink' for DPN, and through control of the relative humidity during inking and writing with the coated AFM tip. Patterned areas with an alkoxysilane on glass with DPN are functionalized for subsequent immobilization of fluorescently labelled streptavidin via covalent attachment of biotin was demonstrated[29]. DPN was used to deposit nanostructures of conducting polymers on modified silicon substrates. Two kinds of modified silicon surfaces were used: a (trimethoxysilyl)propyldiethylenetriamine-modified positively charged surface and a piranha solution-generated negatively charged surface. A tip coated with conducting polymer (self-doped sulphonated polyaniline or doped-polypyrrole) was brought into contact with the substrate surface at different locations under ambient conditions for successively longer periods of time, resulting in the conducting polymer molecules being successfully transported from the tip to these charged surfaces[30].

The DPN-generated polymer patterns were stabilized by electrostatic interactions between the charged polymer chains and a functionalized surface. Patterning with DPN using double ink was also demonstrated. In this technique patterns of MHDA and 1-octadecanethiol (ODT) were made on the same Au{111} substrate. The shapes of pre-existing patterns of one ink were not changed by deposition of the other ink[31]. A variation of DPN was also reported, called thermal dip-pen nanolithography (tDPN), that can write molecularly ordered polymer nanostructures with exquisite control of both physical dimensions and orientation. Using tDPN, poly(3-dodecylthiophene) nanostructures were successfully deposited[32] on silicon-oxide surfaces with lateral dimensions below 80 nm.

Another method similar to DPN is the scanning probe-induced cathodic electrografting. Here, the conductive AFM tip loaded with alkyne is electrografted on a hydrogen-terminated silicon surface by giving a positive bias to the tip and negative bias to the surface under ambient condition[33].

Local anodic oxidation

AFM anodization lithography produces protruding oxide patterns on a substrate by faradic current from the cathode tip to the anode substrate. Anodic patterning can be accomplished on a silicon substrate by electrochemical reactions mediated by the scanning probe tip. Electrochemical anodization occurs due to emitted electrons from the tip at the locally scanned area on a silicon substrate in the presence of an atmospheric water column between the tip and the scanned area of the sample. A general reaction scheme of such tip-induced oxidation was proposed by Sugimura and Nakagiri[34]. Equations (1) and (2) describe the anodic reaction that occurs at the substrate surface and eq. (3) shows the cathodic reaction that occurs at the tip[35]:

$$M + xH_2O \rightarrow MO_x + 2x\,H^+ + 2x\,e^-, \qquad (1)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-, \qquad (2)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-. \qquad (3)$$

Thus direct oxidation of hydrogen-passivated silicon substrate[36] and oxidation of molybdenum to molybdenum oxide[37] can be realized by local anodic oxidation. Cavallini et al.[38] have shown parallel writing using the concept of local oxidation nanolithography with DVD as stamp.

Use of SAM as resist

SAM of organic material on silicon substrate was successfully patterned on the nanometre scale using an AFM probe tip and making use of SAM as resist. The process involves raster scanning of an AFM probe tip over a SAM surface using an applied load that is large enough to remove covalently attached organic monolayer from the underlying substrate[39]. Ling et al.[40] have used SAM of n-octadecyltrichlorosilane (OTS) as resist to pattern Au nanoparticles on silicon substrate. This was achieved by scanning probe oxidation of the silicon substrate with OTS monolayer, after which the sample was etched using NH_4F and oxidized with H_2O_2. This was followed by modification with aminopropyltrimethoxysilane (APS) and subsequent treatment with Au nanoparticles resulted in an assembly of Au nanoparticles on the APS modified domain. The steps carried out during the process are depicted in Figure 2. The AFM images in Figure 3 clearly show the Au assembly on the APS modified regions.
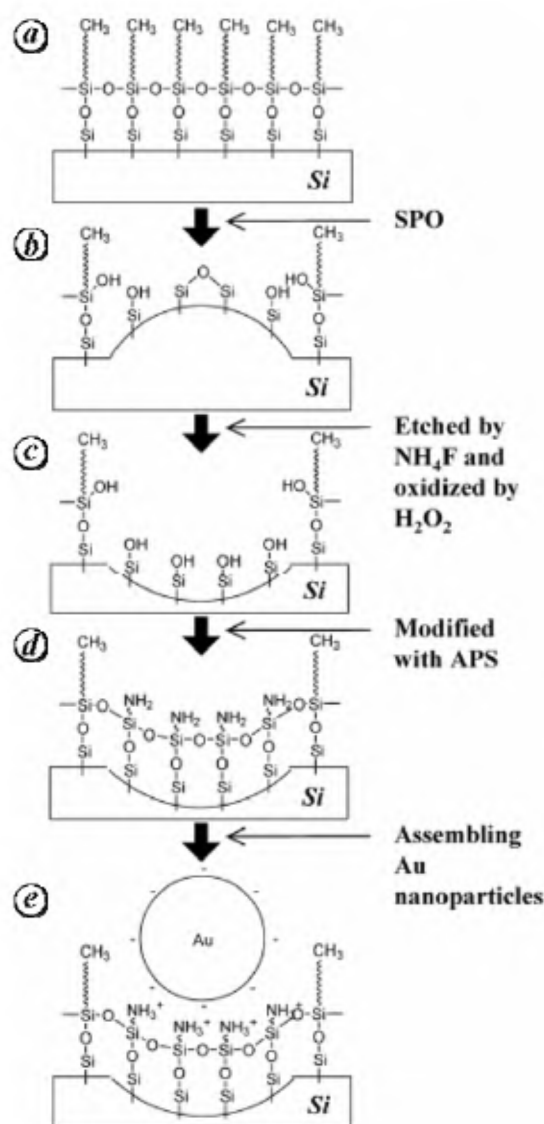
Figure 2. Scheme showing fabricating process on a methyl-terminated silicon substrate of a template homogeneously covered with hydroxyl groups and selective self-assembly of APS and Au nanoparticles. Reprinted with permission. © American Chemical Society.
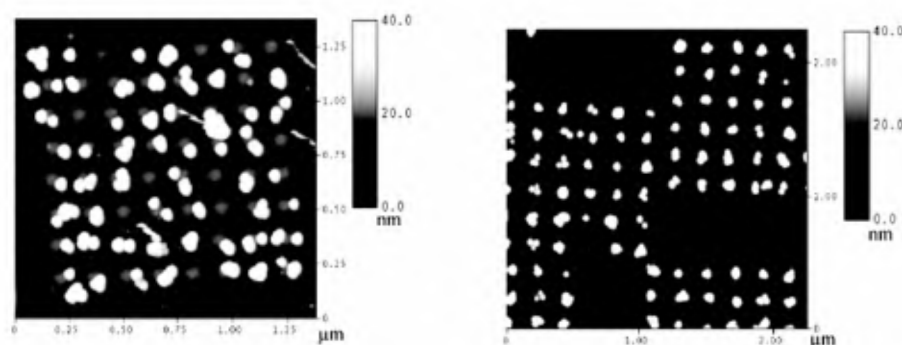
Figure 3. Tapping-mode AFM topographic images of APS-labelled Au nanoparticles on different oxide regions[40]. Reprinted with permission. © American Chemical Society.
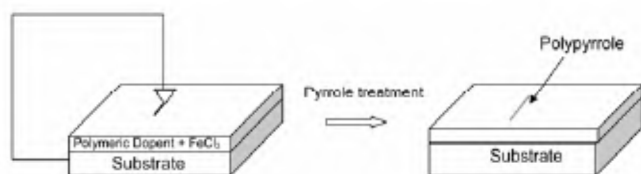
Figure 4. Schematic representation of the process of making nanowires using AFM as a nanomechanical tool for scratching of resist layer to selectively expose the underlying polymeric dopant surface containing the catalyst for polymerization. Treatment with pyrrole monomer results in polymerization in the nanochannels.

Sugimura et al.[41] have also utilized SAM of OTS on silicon wafer to create SiO_2 nanostructures using the local tip-induced oxidation process. In addition, they have also reported a functionalization method by introducing a fluoroalkyl silane. Sugimura and Nakagiri[34] also reported application of the same technique to create nanostructured gold patterns on the surface. In this technique, a silicon wafer with an alkyl silane was locally oxidized to create SiO_2 nanopatterns. Then the SiO_2 was removed by treatment with 0.5% HF. Finally, gold was introduced to the pattern in an electroless plating bath.

The oxidative removal of SAM has also been studied for ODT on gold by Zhao et al.[42], who reported that thiol can be selectively removed from the gold substrate using the AFM tip by applying a bias voltage. Other tip-induced methods include using the AFM tip as a nanomechanical tool to selectively remove the resist layer, such as polymethylmethacrylate, to expose the underlying layer containing the polymerization catalyst. Exposure of the structured resist layer to the pyrrole monomer results in polymerization only in the areas where the monomer comes in contact with the catalyst in the nano channel, thus forming a polypyrrole channel[43]. The schematic representation of the process is shown in Figure 4.

Three-dimensional/two-dimensional nanostructures can be constructed using SPL-based nano-grafting in combination with selective surface reactions within SAM resists. First, nanostructures of functionalized thiol SAM were produced using AFM-based nanografting[44]. Then, a new reactant (long-tail alkyl silane) was introduced to be

attached to the reactive termini on the nanoengineered areas, resulting in selective attachment to the 2D nano-structures to form the 3D structure. Nano-patterns serving as an anchor to construct SPL on carbon surface was shown by Brooksby et al.[45]. Thin films are covalently grafted to the carbon substrate via electrochemical reduction of aryl diazonium salt. Then selectively the film is removed by AFM tip followed by use of another modifier which is electrochemically grafted to the exposed surface. Fréchet and co-workers showed SPL in a fluid cell involving field-induced deposition of etch-resistant material generated from organic solvent such as n-octane, toluene, ethyl alcohol and dioxane. Treatment with $NH_4F/H_2O_2/H_2O$ etchant transfers these structures with increased height, indicative of the formation of etch-resistant material produced by field-induced decomposition of the solvent[46].

Constructive nanolithography

All the methods discussed above make use of either scratching, grafting or SAM as resist. In other words, they destroy the ensuing layer to make nanostructures and hence are destructive in nature. Sagiv and co-workers[47,48] have developed a tip-mediated nanolithography technique, which differs conceptually from other SPL techniques that make use of organic monolayers as passive ultrathin resists. This method has been used to create nanopatterns of chemically active groups on a highly ordered monolayer of OTS self-assembled on silicon, via a local electrochemical oxidation process carried out with a conducting scanning force microscope tip converting the surface exposed $-CH_3$ groups of the base monolayer to $-COOH$ sites[48,49]. In this approach, the local electrochemical oxidation is limited to the selective oxidation of only the top groups of the organic monolayer coating. The initial compact structure and molecular organization of the monolayer are thus preserved and hence the name 'constructive nanolithography'. Figure 5 shows the schematic representation of this process.
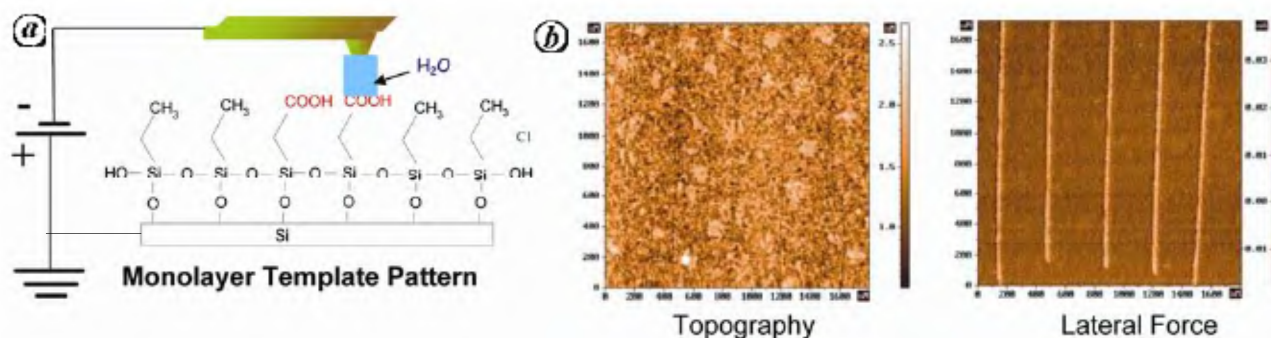
Figure 5. *a*, Schematic representation of constructive nanolithography. *b*, Simultaneously acquired topography and lateral force atomic force images of a series of wire patterns that can be generated using constructive nanolithography.

The brighter region in the lateral force image as shown in Figure 5 *b*, is the polar (–COOH) region on the non-polar (–CH₃) background. It is expected that the reacted regions come brighter (positive) in friction, which is because of the change in polarity of the surface after reaction, as the –COOH surface will show more friction compared to unreacted methylated (–CH₃) surface (Figure 5 *b*). Thus using this technique we can generate polar regions of nanometric dimension in the non-polar methylated background. However, there is a common observation that the patterns come as negative in topography. It is now known that this is an artefact resulting from cross-coupling of topography and friction signals. Using the technique of 'constructive nanolithography', patterns of different shapes and sizes can be fabricated.

Combining constructive nanolithography with self-assembly

The tip-inscribed –COOH patterns made by constructive nanolithography have high chemical, thermal and mechanical stability, which makes them useful as templates in further template-assisted assembly steps. Planned nano-structures of colloidal gold particles, silver particles or semiconductor nanoparticles on silicon can be obtained via hierarchical self-assembly approach, as shown in Figure 6.

The generation of diverse patterned surfaces exposing different functional groups is achieved by the self-assembly of an electrically insulating top monolayer of nonadecyltrichlorosilane (NTS) on the tip-inscribed –COOH sites. The terminal ethylenic groups of the NTS region can be chemically modified to –NH₂ (amine) by photoreacting with formamide which adds a terminal amide group to the hydrocarbon tail of the NTS. Its further reduction with BH₃·THF leads to terminal –NH₂ functionality. This will lead to template-guided surface assembly over the terminal –NH₂ monolayer and site-specific anchoring of gold nanoparticles from a colloidal solution[50], as shown by reaction route (A → B → C → D) in Figure 6. Another possibility comprises of functionalization of

terminal ethylenic groups of the NTS region to –S–H (thiol) top functions. This is achieved by photochemical radical addition of H₂S to the reactive ethylenic functions of NTS and further reduction with BH₃·THF of the fraction of disulphide (–S–S–) groups produced in the process, thus resulting in elevated templates which are copies of the initial inscribed patterns.

Subsequently, similar to the –NH₂ terminated mono-layer, these –SH terminated monolayer template patterns can guide the surface assembly of *ex situ* synthesized clusters such as [Au55] according to the reaction scheme (A → B → E → F) shown in Figure 6. These are well-defined gold 'supramolecules' with a metal core made of only 55 atoms (1.4 nm diameter)[51].

SFM images demonstrating the successful fabrication of template-guided assembly of nanoparticulate gold structures in the form of dots pattern are shown in Figure 7 *a*. The planned organization of [Au55] clusters on the thiol terminated organic template pattern is shown in Figure 7 *b*. Thus in both cases, the anchoring of the gold nanoparticles and gold clusters to the surface is seen to faithfully follow the initial tip-inscribed patterns, thus confirming the validity of the hierarchical step-by-step assembly strategy.

In addition, such templates can also be used in the generation of CdS nanoparticles. This is achieved by chemical oxidation of terminal ethylenic groups of the NTS region to –COOH (carboxylic) by KMnO₄ and KIO₃. Similarly, the bilayer of carboxylic terminated template can guide *in situ* generation of CdS nanoparticles over the carboxylic region by reaction with cadmium salt and passing H₂S gas[48], as shown in reaction scheme A → B → G → H in Figure 6.

Template-controlled self-assembly strategy using the method of tip-induced electrochemical patterning can also be extended to the planned construction of hybrid metal–organic surface nanostructures. In this case starting with a thiol-top-functionalized silane monolayer (TFSM) with silver ions chemisorbed on its outer surface (Ag⁺–TFSM), metallic silver nanoparticles are generated at selected surface sites by tip-induced electrochemical reduction of the surface-bound metal ions[47]. Thus, site-defined reduction
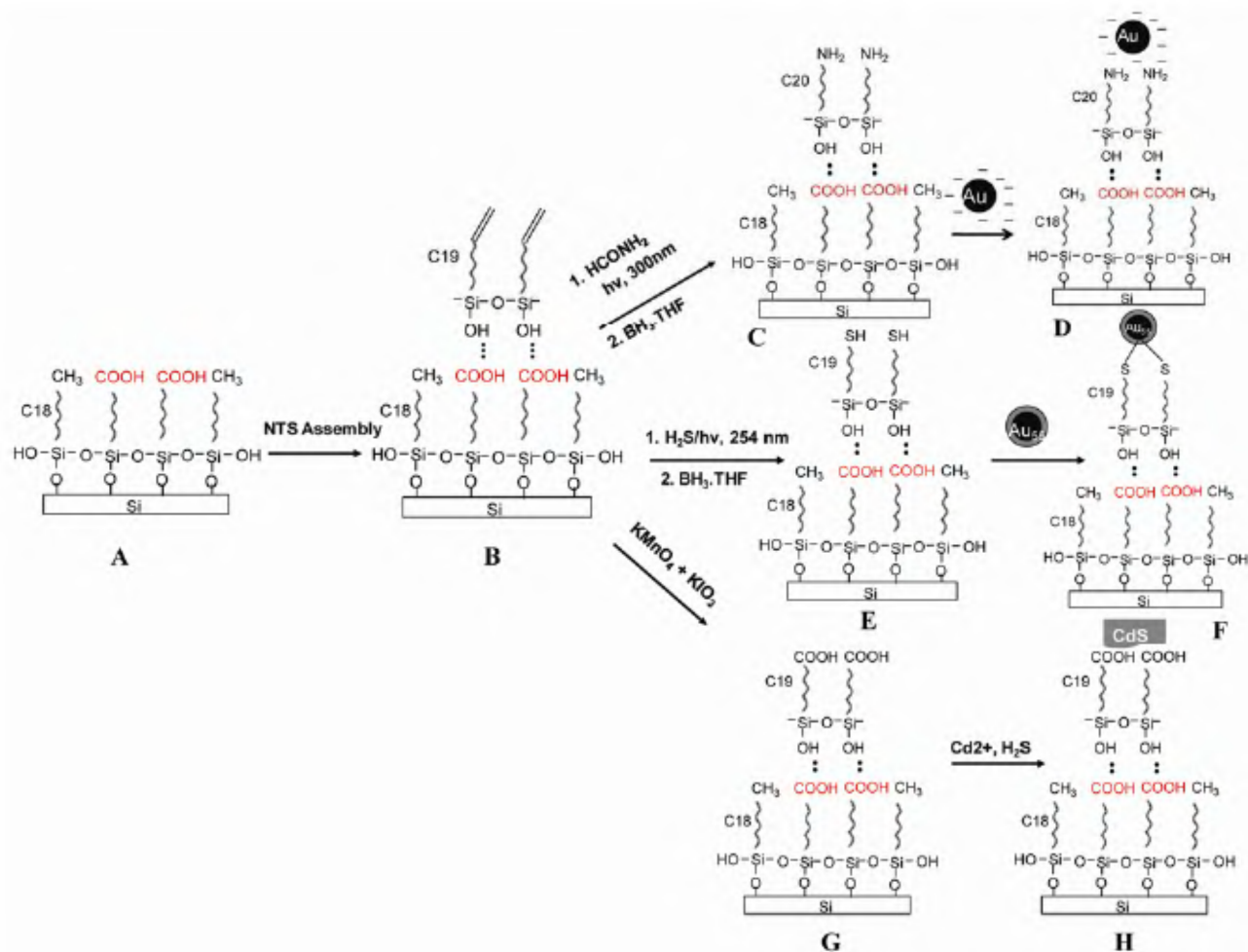
Figure 6. Schematic sketch (not drawn to scale) showing the hierarchical self-assembly of a planned gold nanostructure via template-guided self-assembly of gold nanoparticles over *in situ*-generated top amino functionality (A → B → C → D), gold clusters [Au55] (A → B → E → F) over thiol functionality on a preassembled organosilane bilayer template pattern, and cadmium sulphide nanostructure generated over carboxylic functionalized bilayer pattern (A → B → G → H).

of silver thiolate down to the nanometre-size range can be achieved with the help of a conducting AFM tip. Similar to the other template guided assemblies discussed, silver metal structures are assembled according to a predefined design, by non-destructively imprinting chemical information on the outer surface of a stable, solid-supported organic monolayer that performs the function of an active template for spatial control of the metal self-assembly.

Thus using the concept of such self-patterning approach based on templates with different active/mixed functionality would allow achieving spontaneous phase separation of the binding functions (silver, gold, CdS) within the laterally confined surface domains, enabling fine-tuning of the pattern formation. The construction of such well-defined molecular templates and their use lead to controlling the vertical extensions which can be adjusted with subnanometer precision, offering unique capability to adjusting the distance between surface-anchored nano-objects such as silver, gold and CdS nanoparticles via precise vertical positioning over the substrate surface. This will eventually lead to interesting possibilities for

the advancement of a 3D chemical nanofabrication methodology based on the hierarchical self-assembly of planned multilayer molecular templates.

Wetting-driven self-assembly

The bottom-up nanofabrication strategy can lead to the formation of well-defined template patterns with various functionalities and a precision that can be defined by the height of a single SAM, which emphasizes several advantages in terms of resolution, stability and reproducibility demanded and/or compatibility with other key requirements posed by the engineering of complex nanostructured materials. Furthermore, as stated earlier, these templates are highly stable and robust nanostructures as they can participate in various chemical modifications steps like treatment with different organic solvents, reagents, or concentrated acids, with full preservation of the molecular order and structure. These templates also withstand when such surfaces were imaged with a SFM tip in the contact mode. However, the gene-
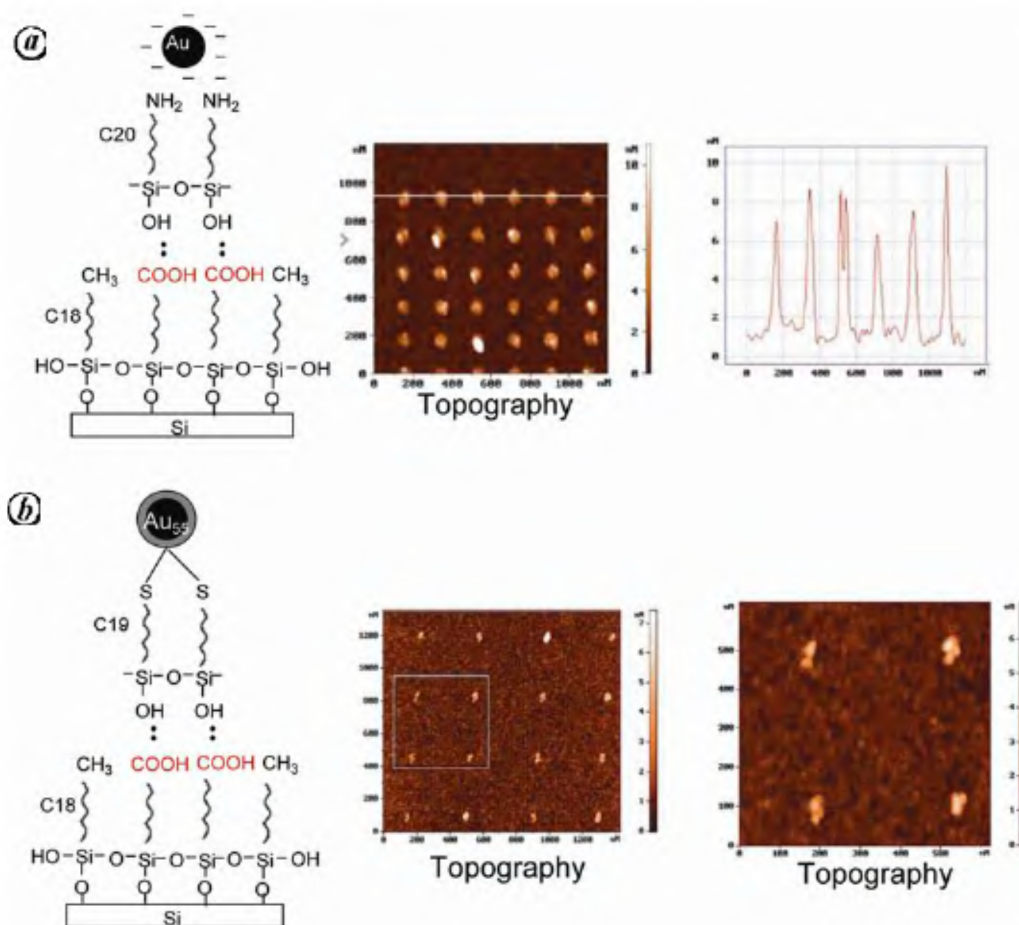
Figure 7. Semi-contact mode AFM topographic images showing (*a*) assembly of gold nanoparticles on amine functionality along with distance–height profile along the marked line (*b*) [Au55] on thiolated bilayer.

ration of such tailor-made patterns requires specially designed molecules, which might be prepared using complex synthetic protocols. Therefore, the materials used for the self-assembly process need to be amphiphilic molecules which have the right structure with a specific anchoring group, that make them suitable for the formation of a closely packed SAM. Moreover, repeated use of the initial inscribed patterns for other new post-assembling processes is limited because of the high structural stability of such overlayer surfaces. Such limitation can be overcome using the wetting-driven self-assembly (WDSA)[52]. In this strategy direct use of the wettability properties of a material is made to fabricate planned metal–organic surface nanostructures. WDSA is based on the methodology of constructive nanolithography to fabricate melt-assembled patterns of various hydrocarbon compounds such as octadecane, eicosene, ODT, lauric acid, etc. This phenomenon is based on wetting-driven immobilization of such compounds on organic monolayer patterns consisting of wettable features surrounded by a non-wettable surface background. Exploiting physisorption rather than specific chemisorption, WDSA is particularly versatile, as any material (not necessary amphiphilic) with any shape, functionality or structure may in

principle be used to create melt-assembled patterns, with only the conditions of having low melting point, being solid at room temperature, non-volatile and having reasonably high surface tension. Using the WDSA approach it may be possible to construct 3D structures with various functionalities without utilizing complex (non-commercial) synthetic precursors such as NTS. Therefore, application of such compounds can become broad, because it is possible to use commercially available materials that are already chemically characterized. While relying on simple, inexpensive and widely applicable chemical methods, the immobilized material having one or more reactive groups can be used as space-confined reactors within which various chemical reactions can take place, thus offering unprecedented new options in surface nanofabrication of planned metal–organic nanostructures due to their structural and composition diversity. The mode of organization, the kinetics of nucleation and growth of metal species assembled within such melt-assembled patterns depend not only on the density of the ion-binding sites but also on the lateral mobility of the metal ions, which may be influenced by the spatial arrangement, density and orientation of the organic moieties. In the previous systems, the metal nanoparticles were *in situ* generated
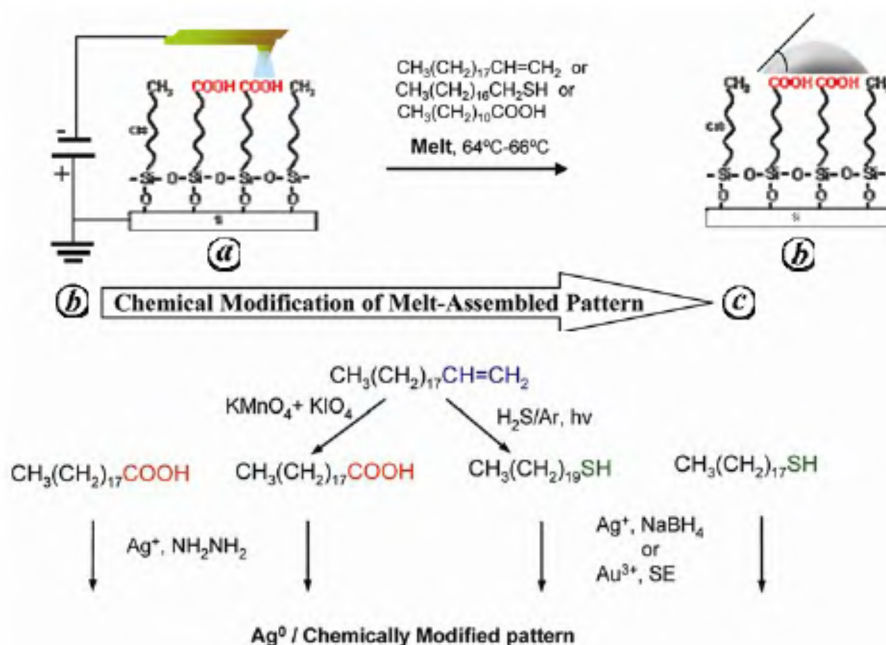
Figure 8. Schematic sketch (drawn not to scale) showcasing the WDSA approach for pattern generation. *a*, Tip-inscribed nanoelectrochemical, non-destructive patterning of self-assembled OTS monolayer on Si, thereby generating wettable nanofeatures on a non-wettable monolayer background. This acts as template for fabricating wetting-driven nanopattern of melt of functionalized material (*b*) and its subsequent chemical modification (*c*). The various reaction routes carried out to generate Ag⁰ assembled on these chemically modified patterns[52] are also listed.
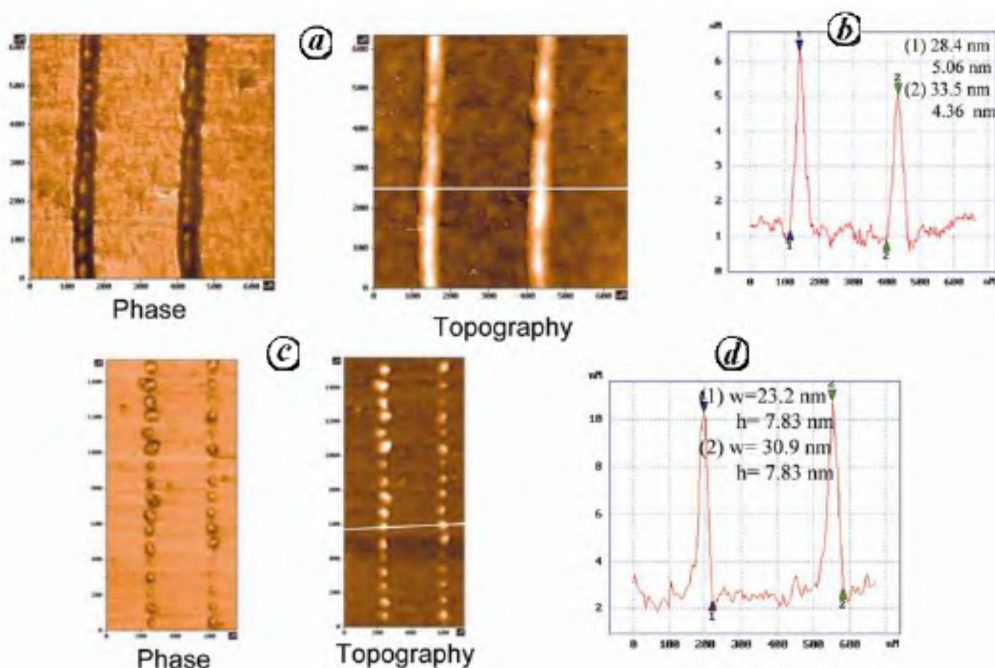
Figure 9. Simultaneous acquired topography as well as phase image after the formation of (*a*) silver wires and (*c*) silver dots over melt-assembled patterns. Distance–height profile along the marked line over the (*b*) silver wire and (*d*) two silver dots.

on top of the organic surface and therefore, any penetrability of the inorganic species through the high-quality structure of the closely packed monolayer template has not been identified. Here, in contrary, the metal nanoparticles can be easily incorporated within the flexible structure of the organic moieties, therefore producing special interconnected metal/organic structures.

The entire process describing the WDSA of hydrocarbon materials (in melt form) on monolayer template patterns and the subsequent synthetic routes are shown in Figure 8. To generate well-defined melt-assembled patterns, the inscribed –COOH sites (Figure 8 *a*) were treated with a neat solution of the hydrocarbon materials (Figure 8 *b*). This was done by immersing the sample for ~10 min in a melt

solution prepared by heating the powder of the desired material (eicosene, ODT, lauric acid, etc.) to 65°C and then slowly retracting with the help of a mechanical lift. The hydrocarbon compounds selectively assembled on the polar regions, leaving the OTS background un-affected. This process is reversible as the material can be dissolved with the help of an organic solvent ($b \Rightarrow a$) and after totally removing it from the surface, the freshly cleaned monolayer template pattern (Figure 8 a) can be reused in other post-assembly processes. The melt-assembled patterns generated in this manner can partici-pate in subsequent chemical modifications steps thus allowing selective manipulation at specific sites, and re-sulting in designed patterns with various functionalities ($b \Rightarrow c$). Starting from a simple ethylenic bond precursor seems to be an easy route to synthesize different chemi-cally modified patterns with terminated functionalities such as –COOH or –SH.

Another possibility to form such surfaces is to use functionalized compounds such as lauric acid or ODT. The subsequent pathways for the *in situ* generation of sil-ver or gold nanoparticles on carboxylic acid or thiol tem-plate patterns take place exclusively on the template-assisted sites, while the OTS-based monolayer remains practically unaffected. Thicker silver films can be grown on such surfaces using the metal-catalysed silver enhan-cer solution that deposits silver only on metal-seeded sites or by the repetitive step-by-step process involved in the chemical reduction of silver or gold ions bound to the top carboxylic acid or thiol groups.

The *in situ*-generated silver particles follow faithfully the chemically modified patterns, thus confirming the validity of the WDSA strategy schematic represented in Figure 8. Some representative SFM images of silver wires generated on chemically modified melt-assembled pattern are shown in Figure 9. Using this method it is possible to fabricate exclusively just one silver particle on each chemically modified patterned dot or obtain silver wires. Thicker silver films can be grown on such surfaces by applying the metal-catalysed silver enhancer solution that deposits silver only on metal-seeded sites.

Conclusion

A combination of nanolithography and surface self-assembly opens up interesting possibilities for confine-ment of diverse selected species such as metal ions, metals, semiconductor nanoparticles and organic compounds in nanoreactors immobilized at predefined surface sites, over which various reaction sequences and reorganization processes may take place. Nanopatterning techniques such as constructive nanolithography are capable of elec-trochemical conversion of the top functional entity with-out affecting the base monolayer, and thus could be used as template for chemical self-assembly as well as WDSA. Thus the chemical nanofabrication strategy combines the

nano-electrochemical pattern inscription on a self-assembled base monolayer with various post-patterning chemical processing operations carried out at different hierarchical levels of complexity. The success of this approach depends on the judicious selection of materials and methods as well as on the precise and careful applica-tion of the selected experimental protocols. For example, to achieve satisfactory selectivity in the immobilization and subsequent chemical processing of the desired species at the desired surface sites, it is necessary to use smooth and highly lyophobic surfaces, which implies assembling highly ordered, defect-free base monolayers.

1. Xia, Y. and Whitesides, G. M., Soft lithography. *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 550–575.
2. Beh, W. S., Kim, I. T., Qin, D., Xia, Y. and Whitesides, G. M., Formation of patterned microstructure of conducting polymers by soft lithography and application in microelectronic device fabrica-tion. *Adv. Mater.*, 1999, **11**, 1038–1048.
3. Yin, Y., Gates, B. and Xia, Y., A soft lithography approach to the fabrication of nanostructures of single crystalline silicon with well defined dimensions and shapes. *Adv. Mater.*, 2000, **12**, 1426–1430.
4. McAlpine, M. C. F., Robin, S. and Lieber, C. M., Nanoimprint lithography for hybrid plastic electronics. *Nano Lett.*, 2003, **3**, 443–445.
5. Lucas, B. D., Kim, J.-S., Chin, C. and Guo, L. J., Nanoimprint li-thography based approach for the fabrication of large-area, uni-formly oriented plasmonic arrays. *Adv. Mater.*, 2008, **20**, 1129–1134.
6. Maury, P., Eschlante, M., Reinhoudt, D. N. and Huskens, J., Directed assembly of nanoparticles onto polymer-imprinted or chemically patterned templates fabricated by nanoimprint litho-graphy. *Adv. Mater.*, 2005, **17**, 2718–2723.
7. Haynes, C. L. M., Adam, D., Smith, M. T., Hulteen, J. C. and Van Duyne, R. P., Angle-resolved nanosphere lithography: manipula-tion of nanoparticle size, shape, and interparticle spacing. *J. Phys. Chem. B*, 2002, **106**, 1898–1902.
8. Ormonde, A. D. H., Erin, C. M., Castillo, J. and Van Duyne, R. P., Nanosphere lithography: fabrication of large-area Ag nanoparticle arrays by convective self-assembly and their characterization by scanning UV–visible extinction spectroscopy. *Langmuir*, 2004, **20**, 6927–6931.
9. Haes, A. J., Zhao, J., Zou, S., Own, C. S., Marks, L. D., Schatz, G. C. and Van Duyne, R. P., Solution-phase, triangular Ag nanotrian-gles fabricated by nanosphere lithography. *J. Phys. Chem. B*, 2005, **109**, 11158–11162.
10. Maoz, R., Cohen, S. R. and Sagiv, J., Nanoelectrochemical patterning of monolayer surfaces: toward spatially defined self-assembly of nanostructures. *Adv. Mater.*, 1999, **11**, 55–61.
11. Lee, K.-B., Park, S.-J., Mirkin, C. A., Smith, J. C. and Mrksich, M., Protein nanoarrays generated by dip pen nanolithography. *Sci-ence*, 2002, **295**, 1702–1705.
12. Lebret, V. *et al.*, Synthesis and characterization of fluorescently doped mesoporous nanoparticles for two-photon excitation. *Chem. Mater.*, 2008, **20**, 2174–2183.
13. Reufer, M., Rojas-Ochoa, L. F., Eiden, S., Saenz, J. J. and Schef-fold, F., Transport of light in amorphous photonic materials. *Appl. Phys. Lett.*, 2007, **91**, 171904/1–171904/3.
14. Lin, S.-Y., Chow, E., Hietala, V., Villeneuve, P. R. and Joan-nopoulos, J. D., Experimental demonstration of guiding and bend-ing of electromagnetic waves in a photonic crystal. *Science*, 1998, **282**, 274–276.
15. Painter, O., Lee, R. K., Scherer, A., Yariv, A., O'Brien, J. D., Dap-kus, P. D. and Kim, I., Two-dimensional photonic band-gap defect mode laser. *Science*, 1999, **284**, 1819–1821.

16. Shaw, G. A., Trethewey, J., Johnson, A. D., Drugan, W. J. and Crone, W. C., Thermomechanical high density data storage in a metallic material via the shape memory effect. *Adv. Mater.*, 2005, **17**, 1123–1127.

17. Gau, H., Hermingaus, S., Lenz, P. and Lipowsky, R., Liquid morphologies on structured surfaces: from microchannels to microchips. *Science*, 1999, **283**, 46–49.

18. Nair, P. R. and Alam, M. A., Screening-limited response of nano-biosensors. *Nano Lett.*, 2008, **8**, 1281–1285.

19. Boussaad, S., Diner, B. A. and Fan, J., Influence of redox molecules on the electronic conductance of single-walled carbon nanotube field-effect transistors: application to chemical and biological sensing. *J. Am. Chem. Soc.*, 2008, **130**, 3780–3787.

20. Liu, J., Mazumdar, D. and Lu, Y., A simple and sensitive 'dipstick' test in serum based on lateral flow separation of aptamer-linked nanostructures. *Angew. Chem., Int. Ed. Engl.*, 2006, **45**, 7955–7959.

21. Yu, C. and Irudayaraj, J., Multiplex biosensor using gold nanorods. *Anal. Chem.*, 2007, **79**, 572–579.

22. Netzer, L. and Sagiv, J., A new approach to construction of artificial monolayer assemblies. *J. Am. Chem. Soc.*, 1983, **105**, 674.

23. Ivanisevic, A. and Markin, C. A., Dip-pen nanolithography on semiconductor surfaces. *J. Am. Chem. Soc.*, 2001, **123**, 7887–7889.

24. Ding, L., Li, Y., Chu, H., Li, X. and Liu, J., Creation of cadmium sulfide nanostructures using AFM dip-pen nanolithography. *J. Phys. Chem. B*, 2005, **109**, 22337–22340.

25. Liu, X., Fu, L., Hong, S., Dravid, V. P. and Mirkin, C. A., Arrays of magnetic nanoparticles patterned via dip-pen nanolithography. *Adv. Mater.*, 2002, **14**, 231–234.

26. Wilson, D. L., Martin, R., Hong, S., Cronin-Golomb, M., Mirkin, C. A. and Kaplan, D. L., Surface organization and nanopatterning of collagen by dip-pen nanolithography. *Proc. Natl. Acad. Sci. USA*, 2001, **98**, 13660–13664.

27. Demers, L. M., Ginger, D. S., Park, S.-J., Li, Z., Chung, S.-W. and Mirkin, C. A., Direct patterning of modified oligonucleotides on metals and insulators by dip-pen nanolithography. *Science*, 2002, **296**, 1836–1838.

28. Su, M., Liu, X., Li, S.-Y., Dravid, V. P. and Mirkin, C. A., Moving beyond molecules: patterning solid-state features via dip-pen nanolithography with sol-based inks. *J. Am. Chem. Soc.*, 2002, **124**, 1560–1561.

29. Jung, H., Kulkarni, R. and Collier, C. P., Dip-pen nanolithography of reactive alkoxysilanes on glass. *J. Am. Chem. Soc.*, 2003, **125**, 12096–12097.

30. Lim, J.-H. and Mirkin, C. A., Electrostatically driven dip-pen nanolithography of conducting polymers. *Adv. Mater.*, 2002, **14**, 1474–1477.

31. Hampton, J. R., Dameron, A. A. and Weiss, P. S., Double-ink dip-pen nanolithography studies elucidate molecular transport. *J. Am. Chem. Soc.*, 2006, **128**, 1648–1653.

32. Yang, M., Sheehan, P. E., King, W. P. and Whitman, L. J., Direct writing of a conducting polymer with molecular-level control of physical dimensions and orientation. *J. Am. Chem. Soc.*, 2006, **128**, 6774–6775.

33. Hurley, P. T., Ribbe, A. E. and Buriak, J. M., Nanopatterning of alkynes on hydrogen-terminated silicon surface by scanning probe-induced cathodic electrografting. *J. Am. Chem. Soc.*, 2003, **125**, 11334–11339.

34. Sugimura, H., Takia, O. and Nakagiri, N., Scanning probe lithography for electrode surface modification. *J. Electroanal. Chem.*, 1999, **473**, 230–234.

35. Service, R. F., Assembling nanocircuits from the bottom up. *Science*, 2001, **293**, 782–785.

36. Tello, M., Garicia, F. and Garcia, R., Line width determination in local oxidation nanolithography of silicon surface. *J. Appl. Phys.*, 2002, **92**, 4075–4079.

37. Rolandi, M., Quate, C. F. and Dai, H., A new scanning probe lithography scheme with a novel metal resist. *Adv. Mater.*, 2002, **14**, 191–194.

38. Cavallini, M., Mei, P., Biscarini, F. and Garcia, R., Parallel writing by local oxidation nanolithography with submicronmeter resolution. *Appl. Phys. Lett.*, 2003, **83**, 5286–5288.

39. Headrick, J. E., Armstrong, M., Cratty, J., Hammond, S., Sheriff, B. A. and Berrie, C. L., Nanoscale patterning of alkyl monolayers on silicon using the atomic force microscope. *Langmuir*, 2005, **21**, 4117–4122.

40. Ling, X., Zhu, X., Zhang, J., Zhu, T., Liu, M., Tong, L. and Liu, Z., Reproducible patterning of single Au nanoparticles on silicon substrates by scanning probe oxidation and self-assembly. *J. Phys. Chem. B*, 2005, **109**, 2657–2665.

41. Sugimura, H., Hanji, T., Hayashi, K. and Takai, O., Surface potential nanopatterning combining alkyl and fluoroalkylsilane self-assembled monolayer fabricated via scanning probe lithography. *Adv. Mater.*, 2002, **14**, 524–526.

42. Zhao, J. and Uosaki, K., A novel nanolithography technique for self-assembled monolayers using a current sensitive atomic force microscope. *Langmuir*, 2001, **17**, 7784–7788.

43. Jahromi, S., Dijkstra, J., van der Vegte, E. and Mostert, B., *In situ* polymerisation of pyrrole in nanochannels produced by means of AFM lithography. *Chem. Phys. Chem.*, 2002, 693–696.

44. Liu, J.-F., Cruchon-Dupeyrat, S., Garno, J. C., Frommer, J. and Liu, G.-Y., Three-dimensional nanostructure construction via nanografting: positive and negative pattern transfer. *Nano Lett.*, 2002, **2**, 937–940.

45. Brooksby, P. A. and Downard, A. J., Nanoscale patterning of flat carbon surface by scanning probe lithography and electrochemistry. *Langmuir*, 2005, **21**, 1672.

46. Suez, I., Backer, S. A. and Fréchet, J. M. J., Generating an etch resistant resist layer from common solvents using scanning probe lithography in a fluid cell. *Nano Lett.*, 2005, **5**, 321–324.

47. Maoz, R., Frydman, E., Cohen, S. R. and Sagiv, J., Constructive nanolithography: site-defined silver self-assembly on nanoelectro-chemically patterned monolayer templates. *Adv. Mater.*, 2000, **12**, 424–429.

48. Hoeppener, S., Maoz, R., Cohen, S. R., Chi, L. F., Fuchs, H. and Sagiv, J., Metal nanoparticles, nanowires and contact electrodes self-assembled on patterned monolayer template – a bottom-up chemical approach. *Adv. Mater.*, 2002, **14**, 1036–1041.

49. Wouters, D., Willems, R., Hoeppener, S., Flipse, C. F. J. and Schubert, U. S., Oxidation conditions for octadecyl trichlorosilane monolayer on silicon: a detail atomic force microscope study of effects of pulse height and duration on the oxidation of the monolayer and the underlying Si substrate. *Adv. Funct. Mater.*, 2005, **15**, 938–944.

50. Liu, S., Maoz, R. and Sagiv, J., Planned nanostructures of colloidal gold via self-assembly on hierarchically assembled organic bilayer template patterns with *in-situ* generated terminal amino functionality. *Nano Lett.*, 2004, **4**, 845–851.

51. Liu, S., Maoz, R., Schmid, G. and Sagiv, J., Template guided self-assembly of [Au55] clusters on nanolithographically defined monolayer patterns. *Nano Lett.*, 2002, **2**, 1055–1060.

52. Chowdhury, D., Maoz, R. and Sagiv, J., Wetting driven self-assembly as a new approach to template-guided fabrication of metal nanopatterns. *Nano Lett.*, 2007, **7**, 1770–1778.