Nano- and Micropatterning by Organic – Inorganic Templating of Hierarchical Self-Assembled Structures

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Miniaturization in electronics through improvements in established "top-down" fabrication techniques is approaching the point where fundamental issues are expected to limit the dramatic increases in computing seen over the past few decades. In aspects of biophysics, biotechnology, and diagnostics, nanostructured interfaces are regarded as valuable tools for the localization of individual ligands designed to test single events or for the construction of hierarchical intracellular micro- and nanoarchitectures by the adhesion of cells.[1] Three essential requisites have to be accomplished for these applications: a) the location and connection of nanosized objects with variable distances from subnanometer to submicrometer, b) pattern uniformity over large surface areas or volumes, and c) control of the pattern geometry, including the assembly of asymmetric structures.

Principally, the top-down approach addresses dimensions of 50 nm (electron-beam lithography) and larger (photolithography). Smaller dimensions down to 10 nm are feasible by electron-beam lithography, but this involves increased efforts which are economically not viable because they are restricted to small surface areas and low-throughput production. For several years wet-chemistry has provided challenging alternatives to expensive clean-room lithographic techniques. The smallest objects, that is, dots or rods of a few nanometres, are synthesized reproducibly using phases of low-molecular weight surfactants. These objects self-assemble into two- and three-dimensional structures through electrostatic, magnetic, and steric interactions as well as through capillary forces upon evaporation of solvents during film formation.[2, 3] The problems arising are the connectivity of the nanoobjects to the macroscopic world, the limited spacings between nanoobjects, and the formation of aperiodic structures. The size range between a few nanometres and 200 nm reflects the gap between top-down approaches and structures made through the pure self-organization of low-molecular-weight species; bridging this size gap offers solutions for overcoming problems of connectivity, breaking pattern symmetry, and noneconomic production aspects. Strategies to bridge this scientific and economically very important size range are addressed through self-assembly of colloidal,[4] macromolecular,[5] or supramolecular units,[6] and thus rely on patterning with periodicities that relate to the molecular weight of the self-organizing molecules. This article presents examples of the latest advances in the application of the self-assembly of macromolecules and colloids, which indeed scale between 5 – 200 nm, overcome symmetry restriction in self-assembly and substrate choice, and allow for inorganic templating of their structure.

Jaeger and co-workers from the University of Chicago demonstrated a method for laterally patterning of metal nanocrystal monolayers onto a solid substrate.[7] In this approach dodecanethiol-ligated gold nanocrystals were synthesized and assembled through both entropic effects and interparticle interactions onto a substrate to form a densely packed film of nanocrystals. The distance between the crystals is determined by steric interactions of the dodecane molecules. The desired pattern was written directly into the monolayer by exposing it to the electron beam of a scanning electron microscope, whereby the organic ligands were stripped from the nanocrystal cores, thus leaving the metal cores to adhere to the substrate. Presumably, this occurs through cleavage of C–H and C–C bonds. In a final washing step unexposed nanocrystals were removed by a solvent to leave the exposed areas of the monolayer firmly anchored to the substrate. Once the ligands are stripped away, the nanocrystals stick strongly to the substrate and are not removable by subsequent washing with solvents. The resolution of the technique depends on the width of the electron beam. The best resolution obtained by the authors was approximately 50 nm, but smaller values should be readily achievable with smaller spot sizes. The fact that the electron beam does not significantly disturb the spatial arrangement of the individual nanocrystals implies that the ordering is essentially controlled by the self-assembly properties of the particles prior to patterning and could be used in other self-organizing, organic – inorganic hybrid systems.

The size of the features fabricated with standard electron-beam lithography is usually much larger than the diameter of the electron beam. Secondary electrons generated by forward scattering and proximity effects increase the exposed volume,

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and the large size of the molecules in the polymeric resists limits the resolution that can be obtained. A further class of materials suitable for ultrahigh-resolution electron-beam patterning are self-assembled monolayers (SAMs), which accumulate chemical functionalities at an interface. SAMs show specific sensitivity to irradiation with electrons. Gölzhäuser, Grunze, and co-workers showed that the nitro groups in SAMs of 4′-nitro-1,1′-biphenyl-4-thiol on gold are converted into amino groups by irradiation with low-energy electrons, while the underlying aromatic layer is dehydrogenated and cross-linked (Figure 1).[8] Sequential exposures to electron beams followed by coupling of electrophilic molecules to the amino-terminated regions allowed for the formation of several chemically different units on a solid interface with molecular resolution (Figure 1).

Pure self-organization of metal nanostructures on surfaces is observed by using domains of diblock copolymers as templates with different adhesion interactions to the metal. Lopes and Jaeger applied a process where one level of self-assembly guides the next (Figure 2).[9] In a first step, ultrathin films of an asymmetric polystyrene-*block*-poly(methylmethacrylate) (PS-*block*-PMMA) diblock copolymer form a regular scaffold of highly anisotropic, stripelike domains. During a second assembly step, the diffusion of metal atoms being evaporated onto the polymer surface to aggregate selectively along the polymer scaffold is guided by differential wetting. Selective decoration of one of the two copolymer domains is already apparent for a wide range of metals and small deposited amounts (film thickness ca. 0.6 nm) immediately after metal deposition. Au and Ag prefer the PS domains, while In, Pb, Sn, and Bi prefer the PMMA domain. Selectivity of nearly 100 % is achieved by warming the system in an inert-gas atmosphere to a temperature that is above the glass temperature of the copolymer. This process leads to a coagulation inside the preferred domain that increases both the size and the separation of the nanoparticles, while the metal diffuses into the domains, perpendicular to the film plane. With the exception of Ag, depositing larger amounts of metal does not fill the domains. Rather than coalescing into continuous, elongated structures of high aspect ratio, the material ignores the template and "jumps the gap" between neighboring domains. Subsequent annealing only reduces the aspect ratio and leads to particles that are more like spheres, but does not reinstate selectivity. Metal density could be increased through repeated deposition of small amounts of metal and short annealing times. This approach produced dense nanochains with a narrow particle size distribution. A second possibility requires a very high mobility contrast

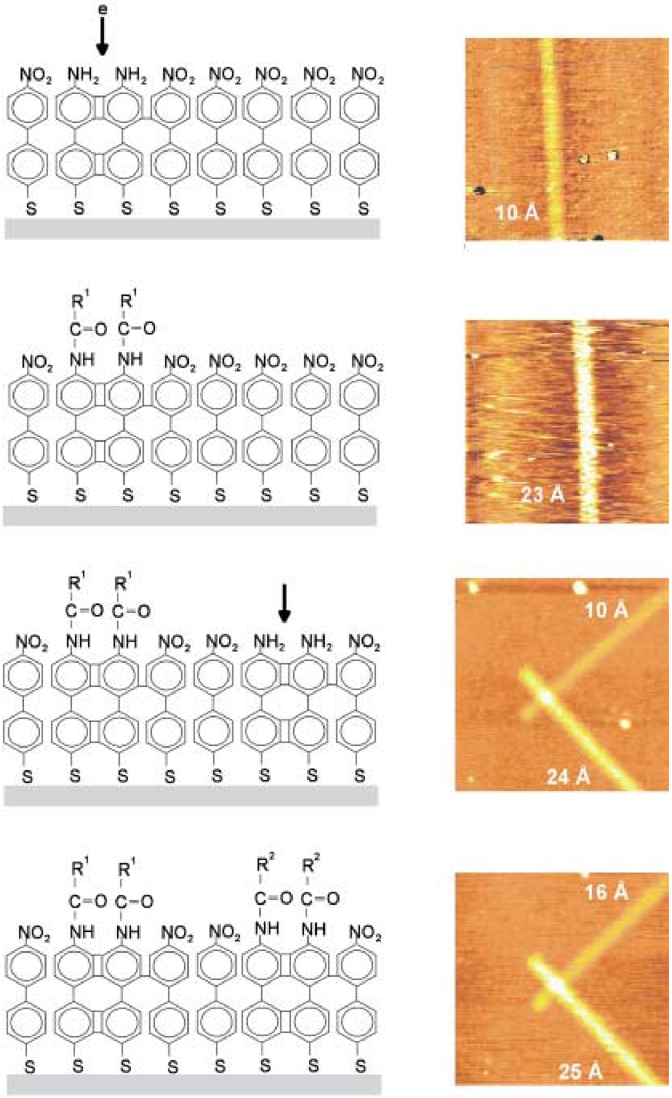

Figure 1. Electron-induced chemical lithography using self-assembled monolayers as a platform for the generation of the pattern. Scanning force microscopy images show the selective binding of acetic acid anhydride ($R^1 = CH_3$) and perfluorobutyric acid ($R^2 = C_3F_7$) onto a SAM platform.

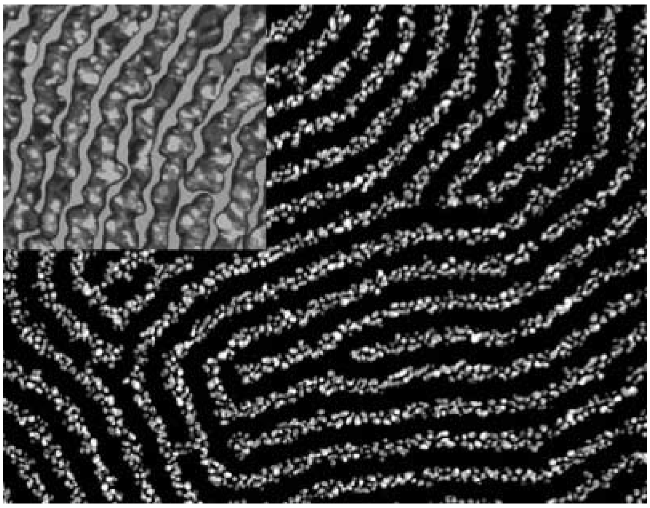

Figure 2. Hierarchically self-assembled metal–polymer structures. Both dense chains of separate nanoparticles and continuous nanowires can be achieved by varying the material parameters. The transmission electron micrograph shows gold nanoparticle chains (light) on a thin PS-*block*-PMMA copolymer film (dark background). The inset shows silver nanowires (dark gray) on the same type of template (light gray background). The center-to-center spacing between adjacent chains or wires is 50 nm, the typical Au particle diameter is 5–8 nm. The large anisotropy and very high dielectric contrast makes these structures suitable for nanogratings, interconnects, and sensor applications, thus opening up new possibilities for guided, large-scale assembly of hybrid nanomaterials and coatings.

between the two copolymer domains, which allows the metal to de-wet one domain and aggregate at a high volume fraction in the other before surface tension drives the aggregate into its final, spherical shape. This is the case with Ag. It readily forms continuous nanowires along the PS domains, which follow 25-nm-wide polymer scaffolds over distances of micrometers without breaks.

Block copolymers and mixtures of homopolymers self-assemble into chemically different domains over large surface areas and on a length scale that is appropriate for many electronic and biological applications. However, for many of these applications it is necessary to have control over the orientation of the domains and also to fabricate an aperiodic pattern. T. P. Russell and co-workers from the University of Massachusetts at Amherst pioneered the application of electrical fields to orient block copolymer domains of different chemical and, hence, different dielectric properties. In addition to block copolymers, homopolymers also respond to electrical fields that are applied either between parallel electrode plates or topographically structured electrodes.[10] This system also allows for the breaking of symmetry, as the resulting polymer pattern follows the topographical structures of the electrodes fabricated by electron-beam or photolithography. The method is based on the fact that dielectric media such as polystyrene experience a force in an electric field gradient. Strong field gradients can produce forces that overcome the surface tension in thin liquid films and induce an instability that produces a characteristic hexagonal order. The application of a laterally varying electric field causes the instability to be focused in the direction of the highest electric field. Hence, this process demonstrates how conventional lithographic techniques can be combined with self-organizing systems. The authors reported patterns with lateral dimensions of 140 nm, but the extension of the technique to pattern replication on scales smaller than 100 nm by using standard lectron beam or photolithography is viable.

The orientation of diblock copolymer domains allows for the formation of ultrahigh-density nanowire arrays. A PS-*block*-PMAA polymer is composed of two materials with different dielectric constants. Thus, an external electrical field orients the polymer domains parallel to the electrical field lines. Russell, Thurn-Albrecht, and co-workers spin-coated an approximately 1-μm thick diblock copolymer film onto a conducting substrate and covered the top of the film with an aluminized kapton (a polyimide) film.[11] The application of an electrical field across the diblock copolymer film causes alignment of cylindrical domains perfectly perpendicular to the electrodes at temperatures above the glass temperature of both polymer components. A major step forward was the use of the aligned domain structures as templates for inorganic species. Exposure of the film with ultraviolet light caused degradation of the PMAA domains and cross-links the polystyrene domains. The degraded PMMA could be removed by rinsing with acetic acid. The resulting nanoporous polystyrene film was optically transparent and contained pores of 14 nm in diameter that span the film thickness. Finally, each pore was filled simultaneously with a continuous Co or Cu nanowire by electrochemical deposition.

Periodic and nonperiodic nanostructures with micrometer spacing have been prepared through the combination of a top-down approach (electron-beam lithography) with the formation and compartmentalization of inorganic components within block copolymer micelles.[12] Electron-beam lithography created channels with a characteristic width greater than 200 nm as a coarse prestructure. Cylindrical block copolymer micelles from organometallic polyferrocene block copolymers were positioned within these structures by means of a self-assembling polymer micelle. The cylindrical micelles are centered within the prepatterned channels and at the edges of prestructured lines as a consequence of capillary effects and steric hindering. Subsequent lifting-off of the resist allows the removal of all the cylindrical micelles with the exception of those that are in direct contact with the underlying substrate. The block copolymer is then removed by plasma etching, which strips the polymer micelle and deposited Fe/Si lines in periodic and aperiodic structures. The lines have a diameter of approximately 5 nm and a length of several micrometers (Figure 3).

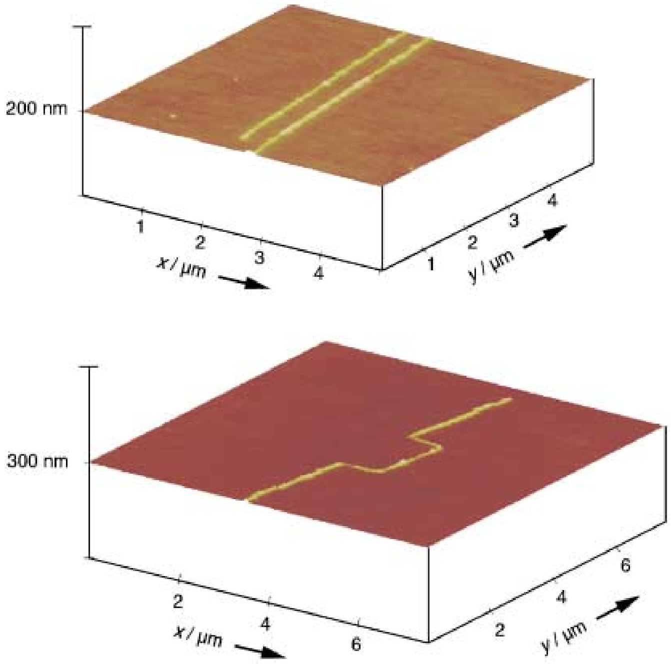

Figure 3. Deposition of Si/Fe-based lines of 5 nm in diameter and several micrometers in length from cylindrical, organometallic polyferrocene block copolymer micelles organized in a 200-nm large prestructure through capillary and steric forces.

The structure of self-organized ultrathin polymer films is usually strongly affected by the interaction of the polymer segments with the interface. Sohn et al. demonstrated that a monomicellar block copolymer film which patterns a mica substrate can be transferred to any other solid substrate by separating the film from the mica substrate with water and floating the micellar film onto a new substrate.[13]

A different length scale in self-organizing structures is addressed with charged colloids. In low ionic suspension media charged colloids arrange to liquid, glassy, or crystalline-like structures as a result of their repulsive electrostatic interactions. The interparticle distance and degree of ordering is a function of the ionic strength and the density of the colloids in suspension. The length of a crystalline pattern can be in the range of several 100 nm. Thus, self-assembly of colloidal crystals enables the preparation of materials whose dimensions lie in the region of the wavelength of visible light, and as such are ideal for photonic crystals. However, a slight change in the ionic strength or any mechanical vibrations might destroy the colloidal structures and, hence, the optical properties. Hempelmann and co-workers demonstrated that the colloidal crystalline structure is not altered if a polyacrylamide hydrogel is polymerized around the colloids.[14] Thus, the colloidal crystal was trapped in the highly cross-linked polymeric hydrogel. The volume between the colloids could then be filled with silver through electrochemical reactions. Accordingly, a colloidal hydrogel was polymerized onto a stainless steel electrode and Ag was electrochemically deposited into the hydrogel from an $AgNO_3$ solution. Finally, the resulting Ag/polymer/colloidal hybrid system was easily removed from the electrode surface (Figure 4). The material showed a pattern periodicity of approximately 160 nm, which makes it suitable, for example, for photonic crystals or as a matrix for catalytic systems.

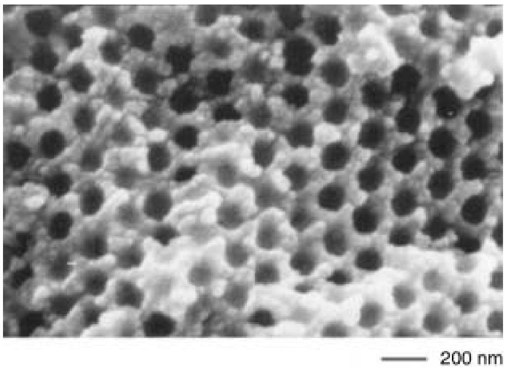

Figure 4. Scanning electron microscopy image of a mesostructured, three-dimensional Ag/polymer/colloidal hybrid material obtained through three-dimensional, inorganic templating of electrostatically organized polymer colloidal crystals.

This Highlight can only summarize a small part of this highly active scientific field concerning the hierarchical self-organization of nano- and microsized objects. Colloids as well as low- and high-molecular-weight molecules self-organize into uniform patterned structures on surfaces and in three dimensions. The pattern of the structure formed is a function of the colloidal or molecular properties and covers dimensions from the subnanometer to the submicrometer range. Even more important is the fact that the combination of conventional lithographic techniques in the submicron range with self-assembling structures in the nanometer range and electric fields result in the controlled alignment of subnanometer structures as well as enabling the breaking of the symmetry intrinsically involved in self-assembly. Thus, a combination of electron-beam or photolithography with the molecular properties mentioned makes patterning in the nanometer range feasible and accessible to a large group of scientists and industry. Most importantly, this is realized without suffering large investments into new clean-room facilities as it is mainly based on wet-chemistry in combination with existing conventional lithographic techniques. The future inclusion of inorganic templating of self-organized structures will make molecular and colloidal lithography highly competitive in the fields of electronics, nanobiotechnology, and diagnostics.

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