Microcontact Deprinting: A Technique to Pattern Gold Nanoparticles

Jingyu Chen, Petra Mela, Martin Möller, and Marga C. Lensen*

DWI e.V. and Institute of Technical and Macromolecular Chemistry, RWTH, Aachen, Pauwelsstrasse 8, D-52056 Aachen, Germany

ARTICLE

ABSTRACT A simple and general patterning technique for inorganic nanoparticles (NPs, *e.g.*, gold NPs) is demonstrated, consisting of the selective lift-off of metal precursor loaded block copolymer micelles. The procedure works as follows: first, a topographically micropatterned polystyrene (PS) stamp is placed in contact with a substrate covered with hexagonally arranged micelles. Then the assembly is heated above the glass transition temperature (T_g) of PS, and finally, the PS stamp is peeled off, removing from the substrate the micelles that were in contact with the protrusions of the stamp. As a result, patterns of micelles either exactly identical to the original or with much smaller features down to submicrometer were obtained. In a subsequent step, the organic material can be removed and the metal precursor reduced by plasma treatment, resulting in patterns of NPs. This technique, denoted as "μ-contact deprinting", provides a fast and inexpensive way to obtain hierarchical patterns of NPs on a wide range of substrates. It is demonstrated that it can even be applied on curved surfaces because of the softness of the PS stamp above its T_g.

KEYWORDS: hierarchical pattern · block copolymer micelles · nanoparticles · stamp deformation

The past decade has witnessed the significant progress in fabricating inorganic nanoparticles with controllable size, shape, and crystalline phase[1−3] for application in catalysis, optics, and electronics.[4,5] In order to optimally exploit their function and to apply them in electronic, photonic, and magnetic devices, one of the current major goals is to find accurate, fast, and low-cost methods to control the NPs' position on substrates.[6−8]

Up until now, many methods to pattern NPs have been successfully developed. For example, the NPs were deposited on selected areas of substrates guided by topographic or chemical patterns.[9−11] Also, by means of the popular μ-contact printing, NPs were printed directly on the substrate.[12,13] In some reports, patterns were written by electron beam or photolithography onto a uniform layer of NPs or their precursors on substrates followed by a development step.[14,15] All these methods can be generally denoted as "top-down" methods. The obtained patterns consisted of unordered, agglomerated, or densely compacted NPs. The feature sizes obtainable by the top-down methods are now approaching their theoretical limits due to the irradiation source and inherent materials' properties. Consequently, the features' reduction takes ever higher cost of production. On the other hand, by "bottom-up" methods, it is possible to arrange NPs down to several nanometers in a certain order. For example, regularly arranged inorganic NPs can be obtained from metal salt-loaded micelles of block copolymers, which self-assemble into a close-packed, hexagonally arranged monolayer when deposited on substrate *via* dip- or spin-coating techniques.[16−18]

The bottom-up and top-down methods can complement each other well, and several processes have been reported to prepare high-resolution patterns of NPs through a combination of them. For example, Yun and co-workers produced micropatterned layers of micelles and NPs through both conventional and soft lithography techniques.[19] However, although the process was fast, the resolution of the pattern is restricted to sizes above micrometer by limitation of the material used. In another kind of "surface-pinning" patterning method, the metal salt-loaded micelles in certain areas were pinned on substrate upon irradiation, while the micelles in the nonexposed areas were washed off.[20−22] However, when UV light was used as irradiation source through a photolithography mask, the resolution reached just several micrometers. On the other hand, when e-beam or focused ion-beam lithography

*Address correspondence to lensen@dwi.rwth-aachen.de.

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was used for higher resolution (*i.e.*, submicrometer to nanometer), the efficiency was low and expensive apparatuses were needed.

In this paper, we report a novel technique to pattern regularly arranged metal NPs by removing the salt-loaded micelles from selected areas on a substrate with a polymer stamp. This technique we denote "μ-contact deprinting". Here, a stamp of polystyrene (PS) with a topographic pattern was placed on the well-arranged poly(styrene)-*block*-poly(2-vinylpyridine) (PS-*b*-P2 VP) micelles on a substrate (*e.g.*, a silicon wafer). At temperatures above the glass transition temperature (T_g) of PS, the PS shells of the micelles adhere to the PS stamp and the whole micelles can be peeled off from the substrate together with the stamp.

Usually, when the pattern reaches submicrometer dimensions, special methods, such as electron beam (e-beam) lithography, are required to fabricate the original silicon masters. The production efficiency is low, and the cost is very high. Here we demonstrate a method avoiding this problem, in which submicrometer patterns of Au NPs on substrates are fabricated with PS stamps with micrometer structures. Contrary to the traditional methods in which usually the patterns on the replica needed to be faithful to the masters and any deformation is avoided, in our technique, we can take advantage of the stamp deformation to create novel patterns. When the PS stamp is heated to a higher temperature, a controllable deformation decreased the spaces between the protrusions on the stamp[23] and produced on the substrate patterns of smaller features, which could reach submicrometer dimensions. Compared with the methods reported previously, this method combines several advantages since it is fast (the whole process takes just several minutes including heating and peeling off), cheap (no expensive professional apparatus is needed), and easy (can be carried out on the benchtop).

RESULTS AND DISCUSSION

Fabrication of Microsized Patterns of Au NPs. In our experiment, the micelles loaded with gold salt were deposited on the silicon wafer in a monomicellar film with a regular, hexagonal packing by dip-coating, following the method reported previously.[16,17] Since the PS-*b*-P2 VP micelles were formed in an apolar organic solvent, the outer shell consisted of hydrophobic PS and the core consisted of hydrophilic P2 VP, with the gold salt coordinated to the P2 VP in the core of the micelle.[22] On the basis of this architecture of the micelles, we designed a process using a stamp (with a topographic pattern) made of PS to fabricate patterns of micelles on a substrate by selectively peeling off the micelles that stick to the stamp. PS stamps of around 0.5 mm thick with topographic pattern were prepared by imprint lithography with PDMS molds at 170 °C. On a hot stage, a PS stamp was positioned on the silicon substrate

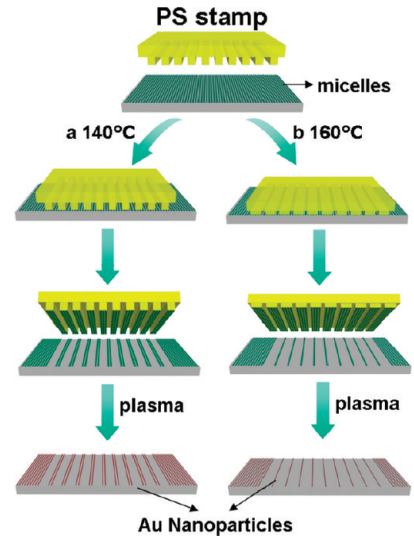

Figure 1. Schematic illustration of the μ-contact deprinting process on a silicon wafer with a monolayer of Au salt-loaded micelles using a PS stamp. Different patterns can be obtained with the same PS stamp at different temperature. (a) At 140 °C, Au salt-loaded micelles are removed from the contacting areas together with the PS stamp, producing micelle patterns with a geometry identical to that of the stamp. (b) At 160 °C, the increased temperature and longer annealing time led to the expansion of the protrusion on the PS stamp. More micelles are removed with the PS stamp, and smaller sized patterns are obtained.

with micelles, and the annealing temperature was set at 140 or 160 °C, as illustrated in Figure 1. After a certain time, the assembly was removed from the hot stage and the PS stamp was separated from the substrate after cooling down to room temperature.

The T_g of PS is about 100 °C, and that of the PS block constituting the shell of micelles is also in this range.[16] After the micelles and the PS stamp were heated above T_g, they adhered to each other quite easily. According to the diffusion theory,[24] at temperatures above T_g, the polymer chains of both the PS stamp and the micelles gained larger mobility. Because of the high compatibility, the polymer chains diffused into each other, leading to strong adhesion. During the whole annealing process, no extra pressure was applied besides the gravity of the stamp, which was enough to ensure the conformal, close contact between the softened stamp and the substrate. When the assembly was removed from the hot stage, in the process of cooling down, the difference in thermal expansion coefficient between the PS and the silicon substrate caused the detachment of the stamp from the substrate. The Au salt-loaded micelles were peeled off together with the PS stamp because of the strong interaction between the PS shell of micelles and the stamp. It should be noted that the heating process has no effect on either the structure or the regular arrangement of the remaining micelles.

Optical microscopy images of the patterned Au salt-loaded micelles on a silicon wafer, with lines of 3 μm in width (distance 10 μm), are shown in Figure 2. Figure 2a is the image of stripes consisting of a mono-

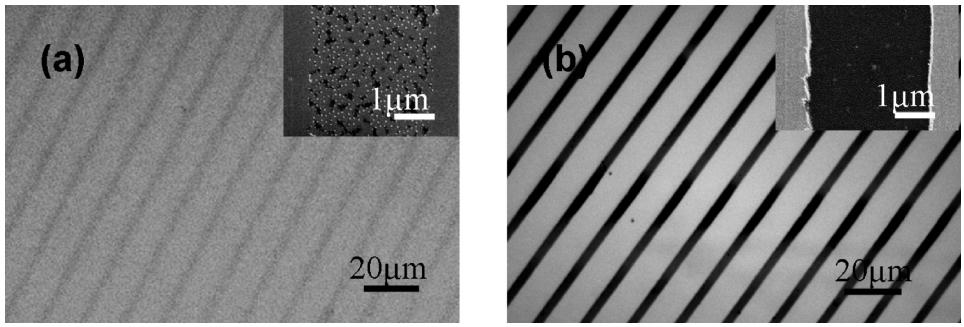

Figure 2. Optical microscopy images of patterned Au salt-loaded block copolymer micelles on a silicon wafer in (a) monolayer and (b) multilayer. The insets are high-resolution SEM images of micelle lines.

layer of micelles. Nevertheless, this method is not limited to monolayers. In the dip-coating process, at the edge of the substrate, the micelles are usually deposited in a multilayer. As shown in Figure 2b, this technique can also be applied to fabricate patterns on multilayers of micelles. The insets are SEM images of the micelle stripes on silicon, which verified that both the monolayer and the multilayer of micelles at the edges of silicon wafers can be removed completely to form patterns with very regular edges and clean interspaces.

The apparent bright spots in the SEM image are NPs since the gold salt in the micelles is reduced by the electron beam during the scanning.

Figure 3a,d shows the SEM images of the PS stamp with topographic patterns of grooves and holes, respectively (as reproduced from PDMS molds with grooves and posts, respectively). Compared with the original silicon master from which the PDMS molds were reproduced, both the size of the grooves and the holes on the PS stamp appear larger around 10%, while the pe-

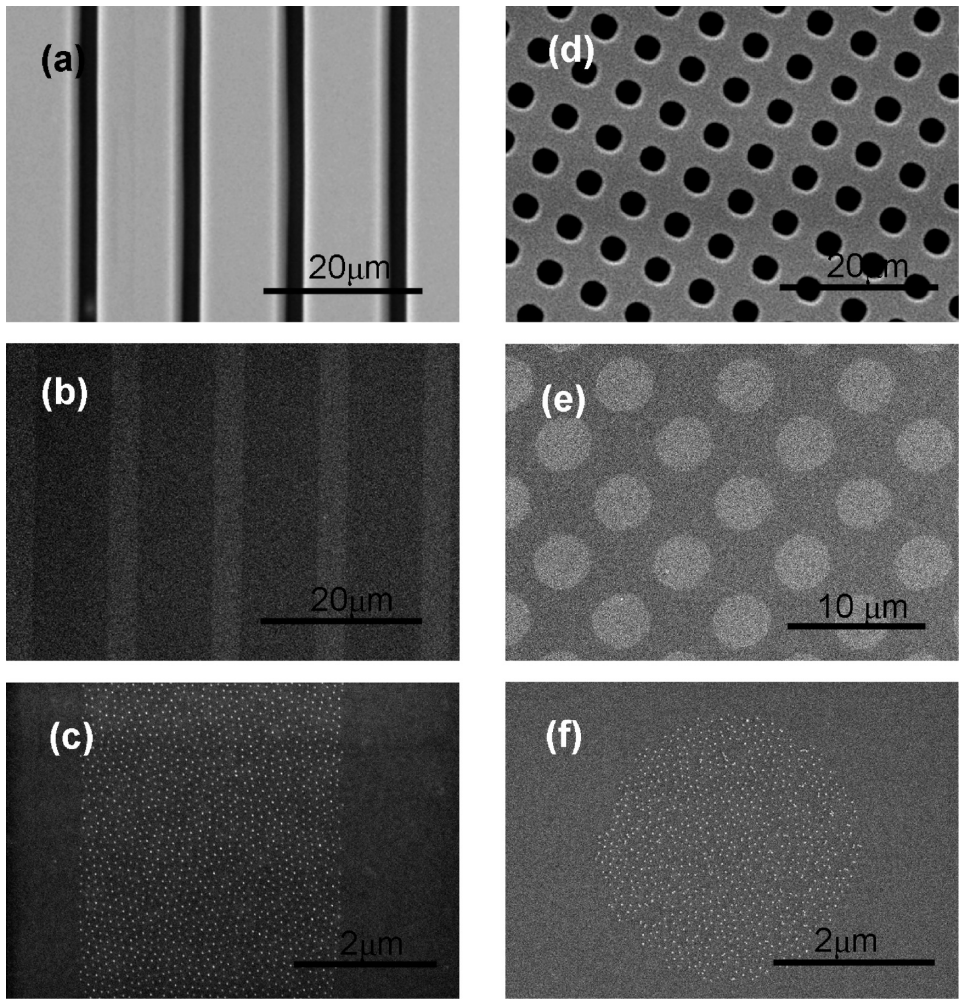

Figure 3. (a,d) SEM images of the PS stamps with stripe and hole patterns. (b,c,e,f) SEM images of patterns on silicon wafer consisting of hexagonally arranged Au NPs (after plasma treatment) obtained *via* deprinting with these PS stamps.

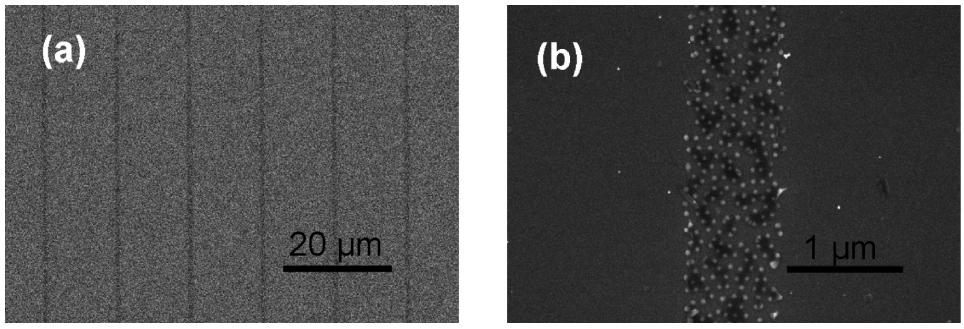

Figure 4. FESEM images of submicrometer patterns of micelles on silicon wafer prepared at 160 °C.

riod of the pattern remained intact. The reason for this is not yet elucidated. In the final step of the deprinting process, by plasma treatment, the polymer material of the micelles was burnt off and the salt in the core was reduced to form Au NPs. Figure 3b,e shows the SEM images of patterned Au NPs: lines of 3.3 μm (13 μm period) and dots of 3.3 μm in diameter (6 μm period), which are exactly identical to the patterns on PS stamps. At higher magnification, it can be seen that the patterns consist of hexagonally arranged Au NPs (Figure 3c,f), which demonstrates that the annealing step did not affect the hexagonal order of the micelles. Again, it can be seen that the edges of these lines are regular, and in the interspace, the micelles have been removed completely with no Au NPs left in the final pattern. In contrast, in the earlier published papers about the pattern obtained from electron beam lithography,[20,22] sometimes a too high energy beam shot the Au NPs out of the micelles' core causing ill-deposition of the Au NPs on the edge.

Under constant force, the degree of deformation of the thermoplastic PS increases with time, and it can be accelerated by a temperature increase. A temperature of 140 °C was selected to prepare the micelle patterns with features exactly faithful to the original masters. At that temperature, the deformation of the protrusions on the stamp was so slow that in a short annealing time its effect on the final pattern was negligible. At lower temperature, the PS stamps failed to peel off the micelles from silicon substrate.

Patterns of Smaller Size. On the other hand, when the temperature was increased, a significant deformation was observed in a short period (*e.g.*, tens of seconds). Here we take the advantage of this property of PS to fabricate patterns of submicrometer sizes by virtue of the controllable deformation of the stamp pattern. This process has been schematically illustrated in Figure 1b. Basically, at a controlled, high temperature (*e.g.*, 160 °C) and a defined annealing time, the lateral dimension of the protrusions of the PS stamp and hence the contact area between stamps and substrate increased. When the PS stamp was removed, more micelles were taken away from a larger area, leaving patterns on the substrate of smaller size compared with the original patterns on the PS stamp. For example, by annealing for 130 s at 160 °C, lines of micelles and eventually Au NPs on silicon wafer with a width of around 800 nm were obtained (Figure 4).

Recently, a method to reduce the feature of thermal plastic nanostructures was reported by Chou's group, in which a pressure of 150 psi was applied to the patterned structures.[23] Differently from their method, here the only force on the PS stamps is the gravity. As for the slices used here, the thickness was around 450 μm and the corresponding pressure applied to the interface was around 6 Pa. With this fixed pressure, the deformation of the stamp and thus the dimensions of micelle patterns can be simply controlled by the annealing time. As demonstrated in Figure 5, from the eventual pattern on the silicon substrate, it can be derived that significant deformation of PS stamps took place already at 30 s. At 150 s, no micelle pattern was left on the substrate anymore, which indicates that at such a high temperature the whole topographic pattern on the stamp melted and disappeared.

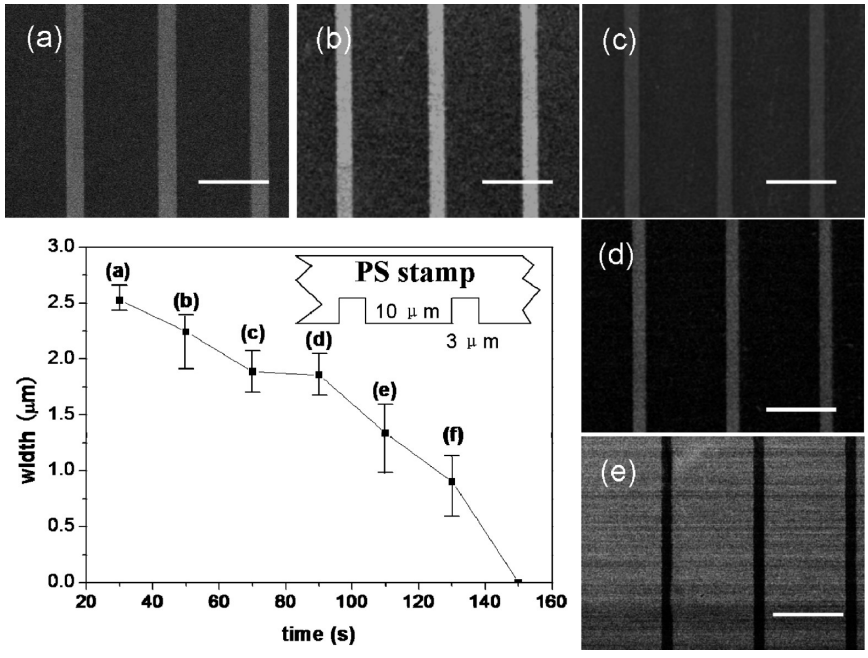

Figure 5. Width of micelle stripe pattern as a function of the annealing time at 160 °C with the PS stamps (450 μm thick, with an original pattern of 10 μm protrusions and 3 μm spacings). (a−e) SEM images of the pattern of micelles corresponding to the data points in the plot. The image of point (f) is shown in Figure 4b. Scale bars represent 10 μm.

Patterning on Curved Surface. The controllable stamp deformation is an application of the viscoelasticity of annealed PS at the microscale. Besides, at the macroscale, it may also be exploited to create novel structures. Since the PS stamps turn soft when heated above T_g, they can be applied not only to flat surfaces but also to curved surfaces. As a proof of principle, a glass pipet was used as a curved surface for patterning. Figure 6 shows the optical microscopy images of the stripes (25 μm in width with 25 μm spacings) on the pipet, in which the pattern of the mold was faithfully reproduced on the curved surface. For it is quite difficult to observe the patterns of Au NPs or micelles on a glass pipet directly by either an optical or an electron microscope, in order to visualize the pattern electroless plating of gold was employed. This technique relies on the fact that the gold only deposits in the areas covered with Au NPs, which serve as seeds.

In summary, we have developed a versatile patterning method to produce hierarchical patterns of inorganic NPs in which the resolution can reach the submicrometer range. Micelles of PS-*b*-P2 VP loaded with gold salt were arranged into hexagonal order in a monolayer on a substrate. With stamps of PS, the micelles were selectively removed at a temperature above T_g of PS. Subsequently, the salt was reduced by plasma treatment resulting in patterns of hexagonally arranged NPs. We denote this technique "μ-contact deprinting". This technique relies on two virtues of the polystyrene: (i) the high compatibility with the outer shell of the micelles; (ii) the viscoelasticity at temperature above the T_g. With the former, the micelles adhered to the stamp and were peeled off, creating micelle and NP patterns with regular edge and clean background. With the latter at microscopic level, the deformation of micrometer structures on the stamp resulted in micelle patterns of submicrometer dimensions. Besides, when applied at the macroscopic level, with the softened stamp, the patterns of micelles on a curved glass surface were successfully fabricated. Thus, we have developed a very adequate technique to manipulate nanomaterials, potentially low-cost, highly efficient, available to large area and applicable on any substrate, including nonconductive and curved ones. Compared with the EBL, which can only be used on conductive substrates, our technique greatly enlarges the application area. Here we employed Au NPs as a particular example, but the NPs can also be prepared from other metals, metal oxides and (other) semiconductor materials, determined by the precursors loaded in the core of the micelles and eventual post patterning treatments. This novel patterning technique covers many length scales, from submicrometer to the macroscale and is a useful platform for nanobiotechnology research. In our further study, these hierarchically patterned NPs will be used as anchors to bind biofunctional molecules for the research on cells, for biosensing applications, or as catalysts for the growth of 1D semiconductor nanomaterials.

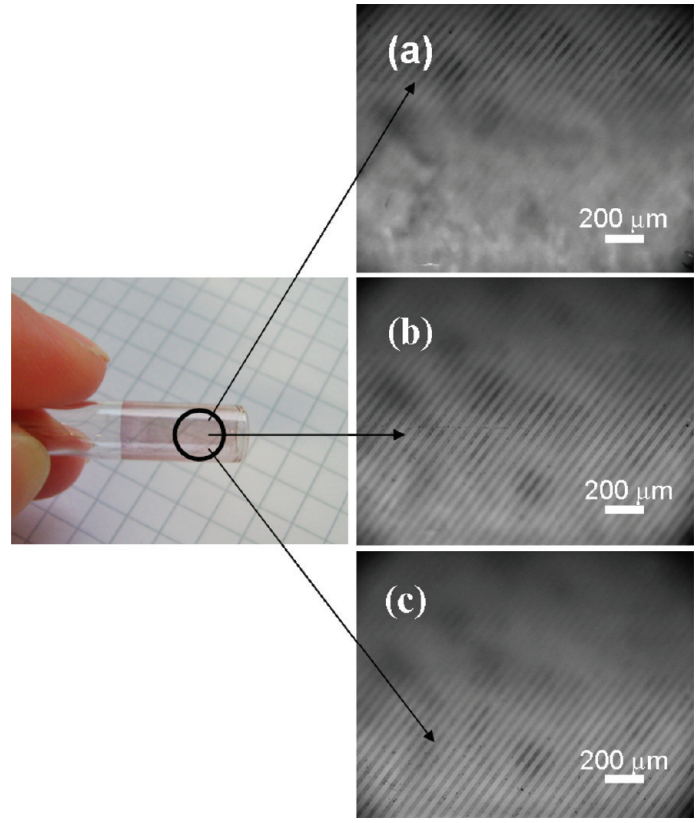

Figure 6. Optical microscopy images of gold stripes on a pipet surface as formed by electroless plating with the patterned Au NPs as seeds. The circle on the left photograph marks the area where the pattern was formed. (a−c) Images focusing on different points of the curved surface. The edge of gold layer on the pipet that can be seen by the naked eye corresponds to the front of micelles in the dip-coating process.

EXPERIMENTAL SECTION

Micelles and Dip-Coating. Au salt-loaded micelles were deposited on silicon wafers following the method reported in detail previously.[16,17] Briefly, PS_{1350}-*block*-P2 VP_{400} was dissolved in dry toluene (5 mg/mL), and the solution was stirred for 48 h to allow micelle formation. Gold(III) chloride, $HAuCl_4 \bullet 3H_2O$ (Aldrich), was added to the solution (0.3 equiv of Au(III) per pyridine unit) and stirred for another 24 h in the dark to load the Au salt in the cores of the micelles. Silicon wafers (Crystec) were cut into small pieces (typically 2 × 1 cm^2) and washed in acetone, water, and isopropyl alcohol under ultrasonication and dried in N_2 flow. The Au salt-loaded micelles were deposited on the silicon wafer by immersing the substrate into the solution and retracting it at a speed of 10 mm/min.

Fabrication of PS Stamp. PS particles (Aldrich, M_w = 192 000) were melt-pressed at 170 °C into slices of 500 μm thick and about 1 cm in diameter in a foil presser. Then a piece of polydimethylsiloxane (PDMS) mold with micrometer features was placed on the PS slice, and the assembly was heated at 170 °C for 1 min on a hot stage. A small pressure was applied to ensure the close contact. The molds and PS slices were separated after taken out from the hot stage and cooled to room temperature. The final thickness of PS stamps was measured to be 450 μm on average.

μ-Contact Deprinting. A PS stamp was placed on a silicon wafer covered with a monolayer of orderly arranged Au salt-loaded micelles, and the assembly was heated to 140 °C. After 60 s, the assembly was removed from the hot stage, and the PS stamp was separated from the silicon wafer after cooling down. For the preparation of submicrometer patterns, the assembly was heated on a hot stage for a certain time period at 160 °C. Finally, the silicon wafer was then exposed to hydrogen plasma for 1 h (100 W, 0.05 mbar) in a plasma machine (PVA TePla 100) to burn off the polymer micelles and at the same time reduce the salt cores of the micelles to Au NPs.

Electroless Plating. The substrates with patterns of Au NPs were immersed in a solution containing 1 mM hydroxyl ammonium chloride ($NH_2OH{\bullet}HCl$) and 1 mM $HAuCl_4$. After 20 min, the samples were taken out, rinsed with water three times, and dried in air.

Instrumentation. Substrates patterned with Au NPs were examined by field emission scanning electron microscopy (FESEM, Hitachi model S-4800) operated at an acceleration voltage of 5 kV and a working distance of 5−6 mm. Optical microscope images were taken with an Axioplan 2 imaging microscope (Carl Zeiss, Goettingen, Germany). Image analysis software ImageJ (freeware) was used to analyze the dimensions of the patterns.

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REFERENCES AND NOTES

1. Cushing, B. L.; Kolesnichenko, V. L.; O'Connor, C. J. Recent Advances in the Liquid-Phase Syntheses of Inorganic Nanoparticles. *Chem. Rev.* **2004**, *104*, 3893–3946.
2. Hu, X. G.; Dong, S. J. Metal Nanomaterials and Carbon Nanotubes: Synthesis, Functionalization and Potential Applications Towards Electrochemistry. *J. Mater. Chem.* **2008**, *18*, 1279–1295.
3. Tao, A. R.; Habas, S.; Yang, P. D. Shape Control of Colloidal Metal Nanocrystals. *Small* **2008**, *4*, 310–325.
4. Lieber, M. C. Nanoscale Science and Technology: Building a Big Future from Small Things. *MRS Bull.* **2003**, *28*, 486–491.
5. Daniel, M. C.; Astruc, D. Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-Size-Related Properties, and Applications toward Biology, Catalysis, and Nanotechnology. *Chem. Rev.* **2004**, *104*, 293–346.
6. Coe, S.; Woo, W. K.; Bawendi, M.; Bulovic, V. Electroluminescence from Single Monolayers of Nanocrystals in Molecular Organic Devices. *Nature* **2002**, *420*, 800–803.
7. O'Connor, E.; O'Riordan, A.; Doyle, H.; Moynihan, S.; Cuddihy, A.; Redmond, G. Near-Infrared Electroluminescent Devices Based on Colloidal Hgte Quantum Dot Arrays. *Appl. Phys. Lett.* **2005**, *86*, 201114.
8. Talapin, D. V.; Murray, C. B. Pbse Nanocrystal Solids for N- and P-Channel Thin Film Field-Effect Transistors. *Science* **2005**, *310*, 86–89.
9. Mendes, P. M.; Jacke, S.; Critchley, K.; Plaza, J.; Chen, Y.; Nikitin, K.; Palmer, R. E.; Preece, J. A.; Evans, S. D.; Fitzmaurice, D. Gold Nanoparticle Patterning of Silicon Wafers Using Chemical E-Beam Lithography. *Langmuir* **2004**, *20*, 3766–3768.
10. Jacobs, H. O.; Whitesides, G. M. Submicrometer Patterning of Charge in Thin-Film Electrets. *Science* **2001**, *291*, 1763–1766.
11. Cui, Y.; Bjork, M. T.; Liddle, J. A.; Sonnichsen, C.; Boussert, B.; Alivisatos, A. P. Integration of Colloidal Nanocrystals into Lithographically Patterned Devices. *Nano Lett.* **2004**, *4*, 1093–1098.
12. Santhanam, V.; Andres, R. P. Microcontact Printing of Uniform Nanoparticle Arrays. *Nano Lett.* **2004**, *4*, 41–44.
13. Wu, X. C.; Lenhert, S.; Chi, L. F.; Fuchs, H. Interface Interaction Controlled Transport of Cdte Nanoparticles in the Microcontact Printing Process. *Langmuir* **2006**, *22*, 7807–7811.
14. Hamann, H. F.; Woods, S. I.; Sun, S. H. Direct Thermal Patterning of Self-Assembled Nanoparticles. *Nano Lett.* **2003**, *3*, 1643–1645.
15. Corbierre, M. K.; Beerens, J.; Beauvais, J.; Lennox, R. B. Uniform One-Dimensional Arrays of Tunable Gold Nanoparticles with Tunable Interparticle Distances. *Chem. Mater.* **2006**, *18*, 2628–2631.
16. Spatz, J. P.; Mossmer, S.; Hartmann, C.; Moller, M.; Herzog, T.; Krieger, M.; Boyen, H. G.; Ziemann, P.; Kabius, B. Ordered Deposition of Inorganic Clusters from Micellar Block Copolymer Films. *Langmuir* **2000**, *16*, 407–415.
17. Kastle, G.; Boyen, H. G.; Weigl, F.; Lengl, G.; Herzog, T.; Ziemann, P.; Riethmuller, S.; Mayer, O.; Hartmann, C.; Spatz, J. P.; Moller, M.; Ozawa, M.; Banhart, F.; Garnier, M. G.; Oelhafen, P. Micellar Nanoreactors: Preparation and Characterization of Hexagonally Ordered Arrays of Metallic Nanodots. *Adv. Funct. Mater.* **2003**, *13*, 853–861.
18. Bhaviripudi, S.; Qi, J.; Hu, E. L.; Belcher, A. M. Synthesis, Characterization, and Optical Properties of Ordered Arrays of Iii-Nitride Nanocrystals. *Nano Lett.* **2007**, *7*, 3512–3517.
19. Yun, S. H.; Sohn, B. H.; Jung, J. C.; Zin, W. C.; Ree, M.; Park, J. W. Micropatterning of a Single Layer of Nanoparticles by Lithographical Methods with Diblock Copolymer Micelles. *Nanotechnology* **2006**, *17*, 450–454.
20. Glass, R.; Arnold, M.; Blummel, J.; Kuller, A.; Moller, M.; Spatz, J. P. Micro-Nanostructured Interfaces Fabricated by the Use of Inorganic Block Copolymer Micellar Monolayers as Negative Resist for Electron-Beam Lithography. *Adv. Funct. Mater.* **2003**, *13*, 569–575.
21. Gorzolnik, B.; Mela, P.; Moeller, M. Nano-Structured Micropatterns by Combination of Block Copolymer Self-Assembly and UV Photolithography. *Nanotechnology* **2006**, *17*, 5027–5032.
22. Mela, P.; Gorzolnik, B.; Buckins, M.; Mourran, A.; Mayer, J.; Moller, M. Low-Ion-Dose Fib Modification of Monomicellar Layers for the Creation of Highly Ordered Metal Nanodot Arrays. *Small* **2007**, *3*, 1368–1373.
23. Wang, Y.; Liang, X. G.; Liang, Y. X.; Chou, S. Y. Sub-10-nm Wide Trench, Line, and Hole Fabrication Using Pressed Self-Perfection. *Nano Lett.* **2008**, *8*, 1986–1990.
24. Fourche, G. An Overview of the Basic Aspects of Polymer Adhesion 0.1. Fundamentals. *Poly. Eng. Sci.* **1995**, *35*, 957–967.