DNA-directed Printing of Self-assembled Nanoparticle Microarrays

Y. H. Zheng and U. Bach

Department of Materials Engineering, Monash University
Wellington RD, Clayton, Victoria 3800, Australia
Yuanhui.Zheng@ monash.edu and Udo.Bach@monash.edu

ABSTRACT

A Gutenberg-style nanoprinting technique that exploits electrostatic nanoparticle self-assembly and DNA-mediated replication of lithographic microstructures was developed. Printing of gold nanoparticles (AuNPs) from lithographic micropatterns (stamps) was successfully shown. The original micropatterns of the stamps were well replicated. The efficiency of the nanoparticle transfer was dependent on the pressure applied to the stamp and capture substrate during the printing process. High AuNP loading and high transfer yields were observed in this work. This new pattern replication technique offers an opportunity to produce functional devices with complex nanostructures at low cost.

Keywords: gold nanoparticles, DNA, patterns, electrostatic self-assembly, Gutenberg-style printing

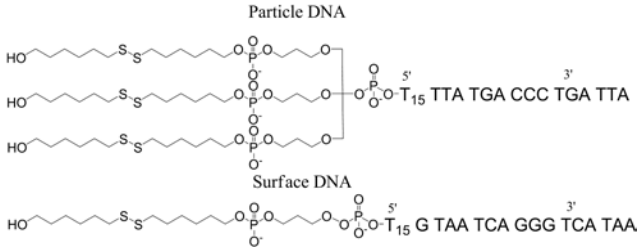
1 INTRODUCTION

Nanostructured materials exhibit unique physical and chemical properties that are different from those of the bulk materials.[1-4] To harness their properties into functional devices, the ability to precisely control the position of the nanostructures on a substrate will be be a key requirement towards their use in advanced applications such as high-sensitivity sensors,[5] optoelectronic circuits,[6] and electronic devices. [7] Conventional top-down lithographic techniques, such as photolithography, electron beam lithography, and ion beam lithography, have been used to produce nanostructures on a solid substrate.[8-10] A general drawback of these top-down lithographic approaches is their high capital, operating and production costs. Novel printing techniques, as alternative nanofabrication tools, could offer a practical solution to this limitation, as they allow to replicate these nanostructures in repetitive printing cycles.[11-14] So far, a number of printing techniques have been developed that exploit the specific affinity of "inks" to a stamp and a capture substrate.[12-16] Physical deposition of a thin metal film (i.e., "ink") onto a patterned poly(dimethylsiloxane) (PDMS) elastomer stamp and then the transfer of the "ink" to a more sticky substrate is a classical example of such an affinity printing method.[15, 16] A self-assembled monolayer (SAM) was usually used as convalent "glues" for the transfer printing.[15] Recently, the concept of printing has been extended from physically deposited metal films to nanoparticulate monolayers.[17-20] Nanoparticles, synthesized through wet-chemical methods, bear exciting optical, electronic and magnetic properties that are often superior to those of physically deposited thin metal nanostructures.[21, 22] Although the fabrication of nanoparticle patterns through nanoprinting techniques has been shown previously, most of these techniques can only provide limited variability of the pattern designs or sacrifice the stamp during the printing process.[17, 20]

Herein, we present a novel affinity-based Gutenberg-style printing approach that allows to fabricate any custom-defined nanoparticle patterns through a repetitive printing process. Electrostatic nanoparticle self-assembly and DNA-mediated nanoparticle transfer are used to replicate micro-features generated by photolithography.

2 EXPERIMETNAL

2.1 Materials



Scheme 1: Chemical structures of DNA used.

Silicon wafers with (100) orientation were purchased from University Wafer. Chromium granules (Cr, 99.5 %) and gold pellets (Au, 99.99%) for vacuum deposition were purchased from Ezzi Vision and AGR Matthey, repectively. Gold nanoparticles (AuNPs, OD=1) were purchased from Ted Pella. Photoresist AZ 5214E and developer AZ 726 were purchased from Clariant GmbH. 2-{2-[2-(2-{2-[2-(1-mercaptoundec-1-yloxy)-ethoxy]-ethoxy}-ethoxy)-ethoxy]-ethoxy}-ethylamine hydrochloride (thiol-PEG-amino) was received from ProChimia. Olionucleotides (see Scheme 1) were purchased from Fidelity Systems and 2-methoxy (polyethyleneoxy)propyl]-trimethoxysilane (PEG-silane) from Gelest Inc. Bis(p-sulfonateophenyl)phenylphosphine dihydrate dipotassium (BSPP) and 6-mercapto-1-hexanol (MCH) were purchased from Sigma-Aldrich and Tween 20 from Bio-Rad Laboratories Pty Ltd. Dipotassium hydrogen phosphate, potassium dihydrogen orthophosphate and ammonium acetate were purchased from Merck.

2.1 Synthesis of DNA-AuNP Conjugates

DNA-AuNP conjugates were synthesized following our previously reported method.[23] 1 ml of 40 nm gold

colloidal solution was concentrated to about 50 µl by centrifugation (3800 rpm, 40 min). 2 µl of 2.5% Tween 20, 10 µl of 100 µM *particle DNA* solution and 10 µl of 100 mM BSPP were added to the AuNP solution, respectively. BSPP was used as a reducing agent to cleave the disulfide functionality on the thiol-terminated DNA strands.[24] The mixture was gently mixed with a vortexer (200 rpm) for approximately 2 h at room temperature, upon which 25 µl of 2.0 M NaCl was added to the mixture. Incubated at room temperature overnight, the DNA-AuNP solution was washed with ultrapure water three times. After the final washing step, the DNA-AuNPs were redispersed in 80 µl of a buffer of 0.05 % Tween 20, 0.5 M NaCl and 20 mM K_2HPO_4/KH_2PO_4 (pH = 7).

2.2 Micropattern Fabrication

Micropatterns in photoresist AZ 5214E were used as received from MiniFAB Pty. Ltd. A film of 2 nm Cr and 10 nm Au was deposited onto the substrates using an Edwards 501 evaporator in a glovebox. The photoresist was removed by immersion into acetone. After the resist lift-off, the substrates were immersed in a mixture of 2.5 µl of PEG-silane, 1.25 ml of toluene and 1 µl of concentrated HCl for 30 min. Following the PEG-silane treatment, the substrates were washed with toluene, ethanol and ultrapure water, and then dried with N_2. Finally, the substrates were immersed into a 5 mM thiol-PEG-amino ethanol solution overnight. The non-reacted thiol-PEG-amino was removed by triple rinsing with ethanol and ultrapure water.

2.3 Capture Substrate Fabrication

A Cr/Au (5/25 nm) layer was deposited onto a silicon substrate (4 × 6 mm^2). Subsequently, the substrate was immersed into a 200 µl solution of 10 mM MCH in ethanol for 4 h, and then triple rinsed with ethanol and ultrapure water. MCH treatment is believed to inhibit horizontal DNA adsorption by forming a monolayer on the Au surface to which the DNA bases have no affinity, thus making them "stand up". Following the MCH treatment, 2 µl of 100 µM *capture DNA* solution, 2 µl of 100 mM BSPP solution, 2.5 µl of 80 mM phosphate buffer (pH = 7) and 3.5 µl of 1.5 M NaCl solution were added onto the substrate. The substrate was then incubated in a humidity chamber at room temperature overnight. Finally, the substrate was triple rinsed with ultrapure water and then dried with N_2.

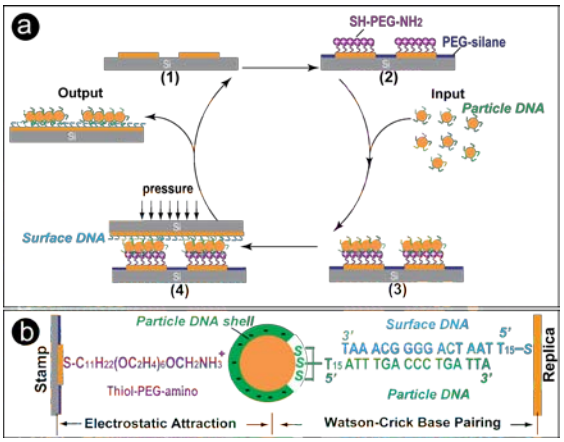
2.4 Self-assembly and printing of DNA-AuNPs

10 µl of 1.5 nM DNA-AuNP conjugate solution was added onto the nanopatterned substrate. The substrate was incubated in a humidity chamber at room temperature for 2 h. Following the DNA-AuNP assembly, the substrate was dipped into ultrapure water several times. Subsequently, the substrate was brought into contact with a capture substrate in the present of 20 µl of phosphate buffer (0.5 M NaCl and 20 mM K_2HPO_4, pH = 9.7) and a pressure of 10-18 N/cm^2 was applied for 2 h. After the pressure was released, the stamp and capture substrate were separated and then dipped into a 0.1 M ammonium acetate solution several times and then dried with N_2.

2.5 Characterizations

All samples were characterized using an Atomic Force Microscope (AFM) from Agilent Technologies (5500 AFM).

3 RESULTS AND DISCUSSION



Scheme 1: (a) Schematic outline of the printing process: (**1**) Cr/Au deposition on a micropatterned substrate (i.e., stamp), (**2**) surface-selective functionalization of the stamp, (**3**) self-assembly of DNA-AuNPs onto the stamp via electrostatic attraction, (**4**) DNA-mediated transfer of the self-assembled AuNPs from the stamp to a complementary DNA modified capture sbustrate; (b) Schematic diagram of the interfacial interactions between the AuNPs and the two substrates.

Scheme 1 illustrates the principle of DNA-mediated Gutenberg-style printing of self-assembled AuNP arrays. A photolithographic micropattern was coated with a thin Cr and Au bilayer. The resist lift-off results in highly ordered gold microarrays (stamp) (**1**). The freshly prepared stamp was surface-selectively functionalized with a monolayer of PEG-silane and thiol-PEG-amino ($SH-C_{11}H_{22}-(OCH_2CH_2)_6OCH_2NH_2$) (**2**). PEG-silane was used to passivate the Si surface via a condensation reaction to block non-specific nanoparticle adsorption. Thiol-PEG-amino was deposited onto the exposed gold surfaces via gold-thiol chemistry. The thiol-PEG-amino monolayer confers positive charges onto the gold surfaces. The stamp was exposed to a solution of DNA-AuNPs in a buffered saline solution to allow for the electrostatic assembly of DNA-AuNPs (**3**). Following the assembly step, the stamp was removed from the DNA-AuNP solution, washed with ultrapure water and dried in air. Non-specifically adsorbed DNA-AuNPs were removed during the washing step. To transfer the self-assembled DNA-AuNPs, the stamp was brought into close contact with a gold-coated Si (100) wafer (i.e. capture substrate), modified with complementary capture DNA, and a pressure (10-18 N/cm^2) was applied in presence of a buffered saline solution (0.5 M NaCl and 20 mM K_2HPO_4 buffer, pH = 9.8)

(**4**), allowing the particle DNA to hybridize with the surface DNA on the capture substrate (Scheme 1b). Subsequently, the pressure was released, yielding the capture substrate carrying a AuNP replica of the original surface micropatterns. The stamp was ready for the following printing cycle.

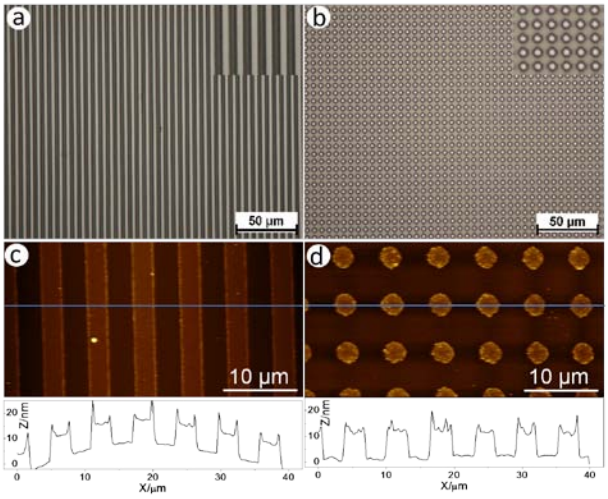


Figure 1: (a, b) Optical microscopy images of the produced micropatterns in the photoresist and (c, d) AFM images and cross-section profiles of the produced gold micropatterns.

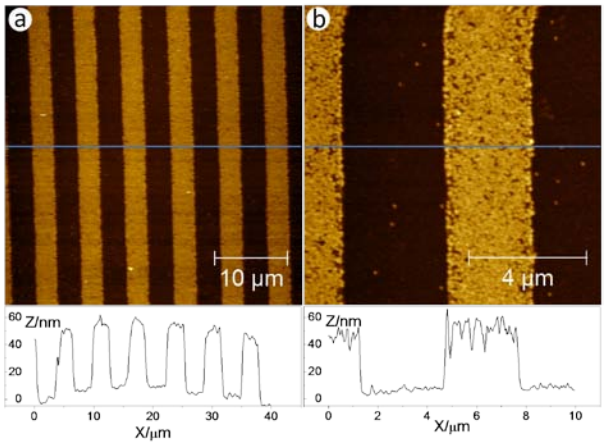


Figure 2: AFM micrographs and cross-section profiles of the gold microwire patterns after the DNA-AuNP loading.

Typical optical microscopy images of the micropatterns produced in the photoresist are displayed in Figure 1a and b. Two different microfeatures, microwires and microdisks, on silicon substrates were fabricated. The patterned surface area is 4×3 mm^2. The microwires are 3µm wide and 3 mm long and the microdisks show a 3 µm diameter. The edge-to-edge distance of two adjacent microfeatures is about 3 µm. Gold micropatterns, fabricated through a sequence of Cr and Au deposition and resist lift-off (see Experimental), are displayed in Figure 1c and d. The height of the microfeatures is approximately 12 nm.

Figure 2 displays representative AFM micrographs and their corresponding cross-section profiles of the produced gold microwire patterns following the AuNP self-assembly. A dense monolayer of DNA-AuNPs is immobilized on the gold microwires, as shown in Figure 2. This is attributed to the electrostatic attraction between the negatively charged DNA-AuNPs and the gold surface, to which the SAM of thiol-PEG-amino confers a net positive surface charge.[25] Few non-specifically adsorbed DNA-AuNPs were observed on the PEGylated silicon surface. The cross-section profiles show that the height of the microwires after DNA-AuNP loading is in a range of 50-55 nm.

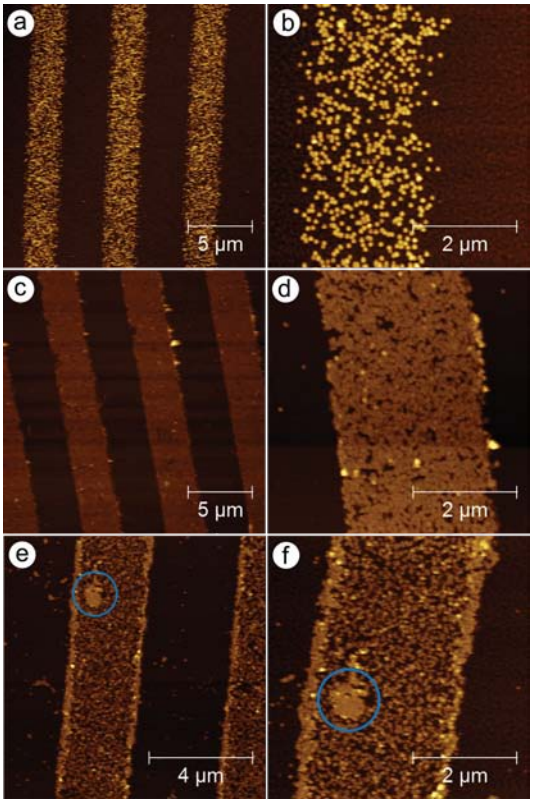


Figure 3: AFM micrographs of the printed nanoparticle microwires obtained at different pressuers: (a) 10 N/cm^2, (b) 15 N/cm^2 and (c) 18 N/cm^2.

Three micropatterned substrates, consisting of an array of gold microwires, were used as stamps to study the effect of presure on the nanoparticle transfer yield. Figure 3 displays AFM micrographs of the printed nanoparticle microwires obtained at different presures. The AFM images shows the successfully transferred DNA-AuNP microwires, as well as the typical grainy structure of the underlying evaporated Au layers. The AuNP transfer yield is dependent on the presure applied to the stamp and capture substrate. When a presure of 10 N/cm^2 was applied, roughly 25% of AuNPs on the stamp were transferred onto the capture substrate (Figure 3a and b). When the presure was increased to 15 N/cm^2, almost all AuNPs was tranferred onto the capture substrate (Figure 3c and d). When the presure was further increased to 18 N/cm^2, the majority of DNA-AuNPs as well as some of the evaporated Au layer

(highlighted with circles) originating from the stamp was transferred onto the capture substrate (Figure 3 e and f).

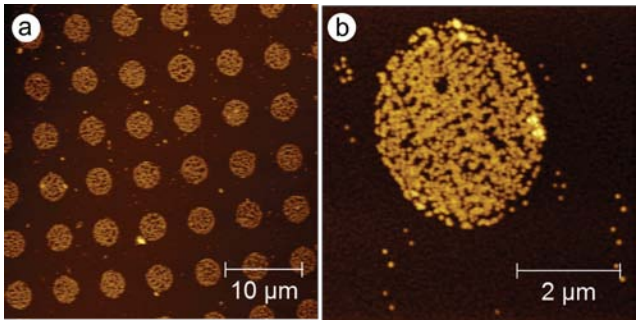


Figure 4: AFM images of the printed AuNP microdisks on a capture substate obtained at a pressure of 15 N/cm^2.

To validate the feasibility of printing other features, a stamp that consists of a regular array of lithographically defined Au microdisks on a silicon wafer (Figure 1d) was used for the self-assembly and printing processes described in Scheme 1. An optimized pressure of 15 N/cm^2 was used for the AuNP printing. Figure 4 shows typical AFM images of the micropattern after its successful transfer to a capture substrate. The original microdisk structure of the stamp is well replicated, as displayed in Figure 4.

4 CONLUSIONS

In summary, we have demonstrated the feasibility of a DNA-mediated Gutenberg-style nanoprinting strategy that uses chemically modified surfaces for the selective adsorption and transfer of nanoparticles from a lithographically patterned stamp to a capture substrate. This new pattern replication approach combines the conventional top-down lithographic techniques with (1) the low-cost and high throughput advantages of nanoprinting techniques, (2) the programmability of DNA-directed pattern transfer, and (3) the extraordinary material properties of wet-chemically synthesized nanomaterials, into one nanofabrication process. Printing of 40 nm gold nanoparticles from micropatterned stamps was successfully shown. The original patterned structures of the stamps were well replicated. The nanoparticle transfer yields are dependent on the pressure apllied during the printing process. High nanoparticle loading and high transfer yields were obtained at a pressure of 15 N/cm^2.

ACKNOWLEDGEMENT

This project was supported by the Australian Research Council (DP0665223, LE0883019).

REFERENCES

[1] C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles*; John Wiley & Sons: New York, 1983.

[2] P. Buffat and J. P. Borel, Phys. Rev. A 13, 2287-2298, 1976.

[3] R. P. Andres, J. D. Bielefeld, J. I. Henderson, D. B. Janes, V. R. Kolagunta, C. P. Kubiak, W. J. Mahoney, R. G. Osifchin, Science 273,1690-1693, 1996.

[4] J. Shi, S. Gider, K. Babcock, D. D. Awschalom, Science 271, 937-941, 1996.

[5] J. N. Anker, W. P. Hall, O. Lyandres, N. C. Shah, J. Zhao, R. P. Van Duyne, Nat. Mater. 7, 442-453, 2008.

[6] H. A. Atwater, A. Polman, Nat. Mater. 9, 205-213, 2010.

[7] E. Ozbay, Science 311, 189-193, 2006.

[8] J. F. Chang, M. C. Gwinner, M. Caironi, T. Sakanoue, H. Sirringhaus, Adv. Funct. Mater. 20, 2825-2832, 2010.

[9] M. Hentschel, D. Dregely, R. Vogelgesang, H. Giessen, N. Liu 5, 2042-2050, 2011.

[10] J. P. Adam, J. P. Jamet, J. Ferre, A. Mougin, S. Rohart, R. Weil, E. Bourhis, J. Gierak, Nanotechonology, 21, 445302, 2010.

[11] C. Pina-Hernandez, L.J. Guo, P. F. Fu, ACS Nano 4, 4776-4784, 2010.

[12] H. H. Lin, L. Sun, R. M. Crooks, J. Am. Chem. Soc. 127, 11210-11211, 2005.

[13] Y. Xia, E. Kim, M. Mrksich, G. M. Whitesides, Chem. Mater. 8, 601-603, 1996.

[14] L. Libioulle, A. Bietsch, H. Schmid, B. Michel, E. Delamarche, Langmuir 15, 300-304, 1999.

[15] Y. L. Loo, R. L. Willett, K. W. Baldwin, J. A. Rogers, J. Am. Chem. Soc. 124, 7654-7655, 2002.

[16] E. J. Smythe, M. D. Dickey, G. M. Whitesides, F. Capasso, ACS nano 3, 59-65, 2009.

[17] V. Santhanam, R. P. Andres, Nano Lett. 4, 41-44, 2004.

[18] L. Kim, P. O. Anikeeva, S. A. Coe-Sullivan, J. S. Steckel, M. G. Bawendi, V. Bulović, Nano Lett. 8, 4513-4517, 2008.

[19] N. Pazos-Pérez, W. Ni, A. Schweikart, R. A. Alvarez-Puebla, A. Fery, L. M. Liz-Marzan, Chem. Sci. 1, 174-178, 2010.

[20] T. Kraus, L. Malaquin, H. Schmid, W. Riess, N. D. Spencer, H. Wolf, Nat. Nanotechnol. 2, 570-576, 2007.

[21] H. Ditlbacher, A. Hohenau, D. Wagner, U. Kreibig, M. Rogers, F. Hofer, F. R. Aussenegg, J. R. Krenn, Phys. Rev. Lett. 95, 257403, 2005.

[22] T. Laroche, A. Vial, M. Roussey, M. Appl. Phys. Lett., 91, 123101, 2007.

[23] C. H. Lalander, Y. Zheng, S. Dhuey, S. Cabrini, U. Bach, ACS Nano 4, 6153-6161, 2010.

[24] A.G. Kanaras, *enzymatic manipulation of DNA/gold nanoparticle assemblies*, PhD thesis, The Univesity of Liverpool.

[25] Y. H. Zheng, C. H. Lalander, U. Bach Chem. Commun. 46, 7963-7965, 2010.