Published in final edited form as:

ACS Nano. 2016 March 22; 10(3): 3144–3148. doi:10.1021/acsnano.6b00528.

Hard Transparent Arrays for Polymer Pen Lithography

James L. Hedrick^{†,‡,§,||,¶}, Keith A. Brown^{‡,§,||,¶}, Edward J. Kluender^{‡,⊥}, Maria D. Cabezas^{‡,§}, Peng-Cheng Chen^{‡,⊥}, and Chad A. Mirkin^{†,‡,§,⊥,*}

[†]Department of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States

[‡]International Institute for Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States

[§]Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States

[⊥]Department of Materials Science and Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States

^{||}Mechanical Engineering and Materials Science & Engineering, Boston University, 110 Cummington Mall, Boston, Massachusetts 02215, United States

Abstract

Patterning nanoscale features across macroscopic areas is challenging due to the vast range of length scales that must be addressed. With polymer pen lithography, arrays of thousands of elastomeric pyramidal pens can be used to write features across centimeter-scales, but deformation of the soft pens limits resolution and minimum feature pitch, especially with polymeric inks. Here, we show that by coating polymer pen arrays with a ~175 nm silica layer, the resulting hard transparent arrays exhibit a force-independent contact area that improves their patterning capability by reducing the minimum feature size (~40 nm), minimum feature pitch (<200 nm for polymers), and pen to pen variation. With these new arrays, patterns with as many as 5.9 billion features in a 14.5 cm² area were written using a four hundred thousand pyramid pen array. Furthermore, a new method is demonstrated for patterning macroscopic feature size gradients that vary in feature diameter by a factor of 4. Ultimately, this form of polymer pen lithography allows for patterning with the resolution of dip-pen nanolithography across centimeter scales using simple and inexpensive pen arrays. The high resolution and density afforded by this technique position it as a broad-based discovery tool for the field of nanocombinatorics.

Graphical abstract

*Corresponding Author. ; Email: chadnano@northwestern.edu

†J.L.H. and K.A.B.: Co-first authors.

The authors declare the following competing financial interest(s): CM has financial interests in/relative to Tera-Print, LLC which could potentially benefit from the outcomes of this research.

Keywords

atomic force microscopy; scanning probe lithography; dip-pen nanolithography; polymer pen lithography; polydimethylsiloxane; plasma-enhanced chemical vapor deposition

Polymer pen lithography (PPL) was invented specifically to address the challenge of depositing soft materials over large areas with nanoscale resolution.^{1,2} It is a cantilever-free scanning probe technique that relies upon an array of elastomeric pyramidal pens, held in a plane by an elastomeric film resting on a rigid transparent backing, to deposit nanoscale features in a massively parallel format across centimeter-scale areas. When each pen comes into contact with a surface to be patterned, it deforms in a manner that can be conceptually separated into (1) a tip deformation that increases the tip-sample contact area and (2) a support deformation that does not change the tip-sample contact area. While the increase of contact-area upon deformation is useful as a means to vary feature size,³⁻⁵ it limits the minimum achievable feature size and sensitizes patterning to variations in pen array height.⁶ As a result, the minimum feature size achieved by PPL is larger than the smallest features written by its cantilever-based predecessor dip-pen nanolithography (DPN) by a factor of ~ 3 .⁶⁻¹³ The dependence of feature size on tip-sample force further limits pattern uniformity because of (1) uncertainty in knowing the tip-sample height and (2) variation of tip height across the array. While both of these factors are reported to be under ~ 250 nm, there is nearly a 1:1 relationship between extension and feature size, so this effect can be quite significant when considering the desire to write large scale arrays of submicrometer features.^{6,14,15}

Interestingly, if the elastomeric pens are replaced with rigid silicon pens (while retaining the elastomeric backing film), force-independent patterning is possible.^{16,17} This technique, known as hard-tip, soft-spring lithography (HSL), offers an $8\text{ }\mu\text{m}$ range in extension over which the feature size does not change. The drawback to HSL is that making each pen array consumes a specialty $50\text{ }\mu\text{m}$ thick Si wafer, in contrast to PPL which utilizes pen arrays that can be molded nearly indefinitely from a single Si mold. Additionally, HSL pens are not transparent, which precludes their use for patterning with energy *via* optical methods.^{18,19} Other noteworthy attempts to improve resolution of PPL have relied on using pen arrays composed of other polymers or hard polymer pens on a soft elastomer support.²⁰⁻²² These approaches reduce the feature size dependence on force by at most $\sim 1/4$, but none have produced extension-independent patterning.

Here, a new cantilever-free pen array architecture is presented that affords the ability to write with high resolution in an extension-independent manner using transparent pen arrays that are simple modifications of inexpensive PPL pen arrays. The central hypothesis of this work is that by coating PPL pen arrays with a thin hard layer, the tip of each pyramid will retain its shape during patterning because strain due to tip-sample contact will be absorbed by the elastomeric layer (Scheme 1). Specifically, coating PPL pen arrays composed of polydimethylsiloxane (PDMS) with silica using plasma-enhanced chemical vapor deposition (PECVD) was found as an effective way to construct pen arrays capable of patterning small molecules and polymers at high resolution without dependence on tip-sample contact force.

RESULTS AND DISCUSSION

In principle, the presence of a conformal hard layer could enable pen arrays to write in a consistently high resolution and extension-independent manner. However, depositing a hard material on a soft material is challenging and often results in buckling^{23,25} and delamination.²⁶ To address this problem, a low temperature PECVD process was developed to minimize the degree of thermal expansion that would lead to residual strain between the hard layer and the elastomeric pen array. Specifically, this deposition process was carried out at 200 °C using 900 mTorr with 500 sccm SH₄, 1420 sccm O₂, and 30 W of high frequency power. By performing spectroscopic ellipsometry of films grown on Si wafers, a growth rate of 0.92 ± 0.01 nm/s was extracted with a refractive index of 1.49 ± 0.01 at a wavelength of 630 nm, as expected for silica. While silica films grown on PDMS films could not be measured using ellipsometry due to the buckling pattern that emerged, this periodic buckling pattern itself was used to compute the film thickness (Figure 1a,c).²⁷ By assuming that the modulus of the silica film is the same as bulk silica, the rate of deposition of silica on the PDMS surface was calculated to be 0.55 ± 0.03 nm/s (Figure 1b).

To determine the optimal thickness of silica that would allow for force- independent patterning, five PPL pen arrays were coated with silica films of different thicknesses and subsequently evaluated for their morphology and behavior during tip-sample contact. When the thicknesses were small (<100 nm), the force on the pens during contact caused the thin silica layer to delaminate from the tip (Figure 1e). In contrast, when the thickness was large (>250 nm), the buckling effect was so great that it substantially deformed the pens and perturbed the uniformity of the pen array (Figure 1f). Pen arrays with ~175 nm thick silica films were found to be optimal compromises that mitigated these effects so that the pyramidal shape was retained without delamination (Figure 1d). While CVD-grown silica was found to be robust for patterning, it has been previously noted that exposing a PDMS film to an O₂ plasma forms a silica film on the surface of the PDMS.²⁸ This observation could explain the change in writing performance of PPL pen arrays following repeated exposure to O₂ plasma; however, this approach to deposit silica layers is impractically slow for generating robust hard layers.

To explore the force-dependent feature size of polymer arrays versus hard transparent arrays, 16-mercaptohexadecanoic acid (MHA) features were patterned onto gold whereby each pen wrote 25 individual dots in an array that varied in extension across the pattern with a constant dwell time. MHA was chosen because it is well-known to form monolayers on gold

and has been patterned extensively by PPL and DPN.¹⁰ Features written by polymer arrays were observed using atomic force microscopy (AFM) to be square with edge lengths that depended on extension. The square morphology originates from the deformation of the tips during patterning. In contrast, the features written by hard transparent arrays were found to be independent of tip-sample force over a 5 μm extension range (Figure 2c,d). PPL performed with hard transparent arrays is more reminiscent of conventional DPN, which generates circular features with dwell time-dependent diameters (diffusion-mediated).⁵

While force-independent patterning will allow for more consistent patterns, intentionally varying pen deformation allows one to pattern macroscopic gradients by tilting the pen array with respect to the patterning surface, which enable nanocombinatoric patterns of a gradient of features.^{3,5,29-31} To regain this ability in these hard transparent arrays, it was hypothesized that tilting the array and approaching the surface slowly would result in a positionally dependent tip-sample contact time, giving a gradient of feature sizes as a result of an increase in diffusion time between the tip and substrate. To test this hypothesis, a patterning experiment was performed in which extension was increased over a 5 μm range with a 1.5 $\mu\text{m/s}$ approach and retraction speed. At most, this would result in a ~ 3 s difference in tip-sample contact time for every micrometer difference in extension. Indeed, after patterning, MHA features ranging from 250 nm to 1 μm in a smooth size gradient were observed (Figure 2a,b). This is an important capability as it allows one to contemplate constructing nanocombinatoric arrays for experiments with PPL arrays coated with silica by making gradients of feature sizes.^{3,32}

As polymers comprise an important class of inks, it is important to verify that hard transparent arrays can pattern polymer inks effectively. To test this capability, polymer arrays and hard transparent arrays were used to pattern a square dot array with an extension that varied over 5 μm after being inked with a 5 mg/mL solution of the block copolymer poly(ethylene oxide)-*b*-poly(2-vinylpyridine) (PEO-*b*-P2VP, $M_n = 2.8\text{-}1.5$ kg $\cdot\text{mol}^{-1}$) in water. In this experiment, the approach speed was 100 $\mu\text{m/s}$, which indicates that varying tip extension over a 5 μm range had a negligible effect on the fixed 2.5 s tip-sample contact time. Following patterning, AFM imaging revealed that features written by conventional polymer arrays exhibited a large square contact area while those written by hard transparent arrays had small round contact areas that were independent of extension (Figure 3a,c). Furthermore, as patterning alkanethiols on gold, it was possible to vary the feature size of polymers by changing approach speed. Specifically the tip extension was varied by 4.2 μm while writing a dot array with an approach speed of 3 $\mu\text{m/s}$, resulting in gradients of feature sizes from 40 to 160 nm (Figure 3b,c).

One major and previously undiscussed problem associated with tip deformation is that it can limit feature pitch. While small molecules that covalently bind to the patterning surface are robust after patterning, large molecules that physically adsorb to a surface, such as polyethylene glycol, can be disturbed after patterning because they behave as fluids in the high humidity environment needed for patterning.^{33,34} Because of this phenomenon, if the tip-sample contact diameter is on the order of the feature pitch, the tip will perturb neighboring features when patterning. With polymer arrays, this manifests as a row of features merging into a single large feature. In principle, this would be mitigated with hard

transparent arrays because of the lack of tip deformation. Specifically, by patterning PEO-*b*-P2VP, hard transparent arrays yielded feature pitches of 175 nm with a hexagonal array (Figure 4a,b). By switching from a square pattern array to hexagonal pattern array, the feature density was even further increased by ~15%. The capability of patterning smaller pitches indicates that it is possible to pattern extraordinary numbers of features. Specifically, by patterning 14 641 polymer dots with each of the four hundred thousand pens in a 14.5 cm² array, it was possible to generate a total of 5.9 billion polymer dot features (Figure 4c,d).

CONCLUSIONS

Cantilever-free scanning probe lithography is poised to become an important capability for rapidly performing nanocombinatoric experiments.^{3,30-32} In this work, it is shown that the use of hard transparent arrays allows one to write higher density and more reliable patterns than is possible using polymer pen arrays. While this silica coating was found to render patterning of polymers and small molecules to be force-independent, it also enables a method of writing gradients with force-independent probes. Importantly, hard transparent arrays are a simple postmodification of polymer pen arrays, indicating that the barrier to adoption is extremely small. Silica was chosen as a hard layer for its optical transparency, ease of deposition using low temperature PECVD, and good adhesion with PDMS. Other materials such as silicon nitride, titania, or conductive films such as indium-doped tin oxide could represent interesting coatings for future studies. Also, it would be interesting to explore how the presence of a silica coating influences the durability of pen arrays. Anecdotally, patterning performance was not observed to degrade with routine patterning. While this manuscript has focused on a new pen array architecture that improves the physical patterning performance of cantilever-free scanning probes, a major opportunity for future research is learning how to direct chemistry in an arbitrary fashion at the tip of each probe. When combined with a technique like scanning probe block copolymer lithography,³⁵⁻³⁷ which utilizes PEO-*b*-P2VP and a metallic precursor to direct the on-surface and spatially confined synthesis of metal nanoparticles, one can create high-density nanoparticle arrays with potentially important implications in areas such as plasmonics, nanomagnetism, and catalysis.^{38,39} Ultimately, the ability to directly write billions of discrete features on a surface is a significant advance for nanolithography and could open avenues for using cantilever-free scanning probe lithography as a combinatorial discovery tool.

METHODS/EXPERIMENTS

Materials

Polydimethylsiloxane was made from a 10 to 1 ratio of Sylgard 184 from Dow Corning. 16-Mercaptohexadecanoic acid (MHA) and hexamethyldisilazane were obtained from Sigma-Aldrich. Poly(ethylene oxide)-*b*-poly(2-vinylpyridine) (PEO-*b*-P2VP, Mn = 2.8-*b*-1.5 kg·mol⁻¹) was obtained from Polymer Source. Glass slides (2 in.) were obtained at VWR.

Fabrication

Standard fabrication of PPL arrays were made as previously reported.^{1, 14} PPL arrays were then inserted into PECVD chamber to be coated with silica at 900 mTorr while introducing 500 sccm SH₄ and 1420 sccm O₂ and 30 W of high frequency power for 320 s with a base plate temperature of 200 °C using a STS LpX CVD.

Ink Preparation

Solutions of 10 mM MHA in ethanol and 5 mg/mL of PEO-*b*-P2VP in water were prepared. All arrays were plasma cleaned for 2 min under oxygen at 60 W. The ink solution (150 µL) was spray-coated onto the array using a Harder Steenbeck Infinity CR plus airbrush with a 0.15 mm needle and an Iwata Power Jet Pro IS-975 Dual Piston Compressor at 20 PSI airflow.

Substrate Preparation

PEO-*b*-P2VP-based ink was patterned on silicon wafers that had been vapor-coated in a desiccator for 24 h with hexamethyldisilazane to render it hydrophobic. MHA features were patterned onto Au-coated silicon wafers. These wafers were coated with 5 nm Ti followed by 35 nm Au using a Kurt J. Lesker Co. PVD 75 electron-beam evaporator.

Patterning

Patterning was performed with a Park XE-150 in a humidity control chamber at a relative humidity between 70 and 95% and at room temperature.

Imaging

Atomic force microscope (AFM) measurements were performed on a Dimension Icon (Bruker) to obtain 3D profiles of the patterns. Tapping mode was used for polymeric features and lateral force microscopy was used for MHA features. Images were processed in Nanoscope Analysis. Optical images were taken with a Zeiss Imager.M2m. Images were processed with ImageJ.

Acknowledgments

This material is based upon work supported by the AFOSR Awards FA9550-12-1-0141 and FA9550-12-1-0280, the Air Force Research Laboratory agreement FA8650-15-2-5518, the Center for Cancer Nanotechnology Excellence (CCNE) initiative of the National Institutes of Health (NIH) under Awards U54CA151880 and U54CA199091. J.L.H. was supported by the Department of Defense (DoD) through the National Defense Science & Engineering Graduate Fellowship (NDSEG) Program. K.A.B. acknowledges support from the Northwestern University's International Institute for Nanotechnology (IIN). P.C.C. acknowledges support from the Ryan Fellowship and the IIN. This work utilized Northwestern University Micro/Nano Fabrication Facility (NUFAB), which is supported by the State of Illinois and Northwestern University.

REFERENCES

1. Huo F, Zheng Z, Zheng G, Giam LR, Zhang H, Mirkin CA. Polymer Pen Lithography. *Science*. 2008; 321:1658–1660. [PubMed: 18703709]
2. Braunschweig AB, Huo F, Mirkin CA. Molecular Printing. *Nat. Chem.* 2009; 1:353–358. [PubMed: 21378889]

3. Giam LR, Massich MD, Hao L, Shin Wong L, Mader CC, Mirkin CA. Scanning Probe-Enabled Nanocombinatorics Define the Relationship Between Fibronectin Feature Size and Stem Cell Fate. *Proc. Natl. Acad. Sci. U. S. A.* 2012; 109:4377–4382. [PubMed: 22392973]
4. Zhong X, Bailey NA, Schesing KB, Bian S, Campos LM, Braunschweig AB. Materials for the Preparation of Polymer Pen Lithography Tip Arrays and a Comparison of their Printing Properties. *J. Polym. Sci., Part A: Polym. Chem.* 2013; 51:1533–1539.
5. Liao X, Braunschweig AB, Zheng Z, Mirkin CA. Force- and Time-Dependent Feature Size and Shape Control in Molecular Printing *via* Polymer Pen Lithography. *Small.* 2010; 6:1082–1086. [PubMed: 19859944]
6. Brown K, Eichelsdoerfer D, Shim W, Rasin B, Radha B, Liao X, Schmucker A, Liu G, Mirkin C. A Cantilever-Free Approach to Dot-Matrix Nanoprinting. *Proc. Natl. Acad. Sci. U. S. A.* 2013; 110:12921–12924. [PubMed: 23861495]
7. Weeks BL, Noy A, Miller AE, De Yoreo JJ. Effect of Dissolution Kinetics on Feature Size in Dip-Pen Nanolithography. *Phys. Rev. Lett.* 2002; 88:255505–255509. [PubMed: 12097097]
8. Piner RD, Zhu J, Xu F, Hong S, Mirkin CA. "Dip-Pen" Nanolithography. *Science.* 1999; 283:661–663. [PubMed: 9924019]
9. Ginger DS, Zhang H, Mirkin CA. The Evolution of Dip-Pen Nanolithography. *Angew. Chem., Int. Ed.* 2004; 43:30–45.
10. Salaita K, Wang Y, Mirkin CA. Applications of Dip-Pen Nanolithography. *Nat. Nanotechnol.* 2007; 2:145–155. [PubMed: 18654244]
11. Vega RA, Shen CK, Maspoch D, Robach JG, Lamb RA, Mirkin CA. Monitoring Single-cell Infectivity from Virus-Particle Nanoarrays Fabricated by Parallel Dip-Pen Nanolithography. *Small.* 2007; 3:1482–1485. [PubMed: 17694589]
12. Smith JC, Lee K-B, Wang Q, Finn MG, Johnson JE, Mrksich M, Mirkin CA. Nanopatterning the Chemospecific Immobilization of Cowpea Mosaic Virus Capsid. *Nano Lett.* 2003; 3:883–886.
13. Liu X, Fu L, Hong S, Dravid VP, Mirkin CA. Arrays of Magnetic Nanoparticles Patterned *via* "Dip-Pen" Nanolithography. *Adv. Mater.* 2002; 14:231–234.
14. Eichelsdoerfer DJ, Liao X, Cabezas MD, Morris W, Radha B, Brown KA, Giam LR, Braunschweig AB, Mirkin CA. Large-Area Molecular Patterning with Polymer Pen Lithography. *Nat. Protoc.* 2013; 8:2548–2560. [PubMed: 24263094]
15. Zhou Y, Xie Z, Brown KA, Park DJ, Zhou X, Chen PC, Hirtz M, Lin QY, Dravid VP, Schatz GC, Zheng Z, Mirkin CA. Apertureless Cantilever-Free Pen Arrays for Scanning Photochemical Printing. *Small.* 2015; 11:913–918. [PubMed: 25315252]
16. Shim W, Braunschweig AB, Liao X, Chai J, Lim JK, Zheng G, Mirkin CA. Hard-Tip, Soft-Spring Lithography. *Nature.* 2011; 469:516–520. [PubMed: 21270890]
17. Eichelsdoerfer DJ, Brown KA, Boya R, Shim W, Mirkin CA. Tuning the Spring Constant of Cantilever-Free Tip Arrays. *Nano Lett.* 2013; 13:664–667. [PubMed: 23286875]
18. Liao X, Brown KA, Schmucker AL, Liu G, He S, Shim W, Mirkin CA. Desktop Nanofabrication with Massively Multiplexed Beam Pen Lithography. *Nat. Commun.* 2013; 4:2103–2110. [PubMed: 23868336]
19. Huo F, Zheng G, Liao X, Giam LR, Chai J, Chen X, Shim W, Mirkin CA. Beam Pen Lithography. *Nat. Nanotechnol.* 2010; 5:637–640. [PubMed: 20676088]
20. Xie Z, Shen Y, Zhou X, Yang Y, Tang Q, Miao Q, Su J, Wu H, Zheng Z. Polymer Pen Lithography Using Dual-Elastomer Tip Arrays. *Small.* 2012; 8:2664–2669. [PubMed: 22777920]
21. Schmid H, Michel B. Siloxane Polymers for High-Resolution, High-Accuracy Soft Lithography. *Macromolecules.* 2000; 33:3042–3049.
22. Odom TW, Love JC, Wolfe DB, Paul KE, Whitesides GM. Improved Pattern Transfer in Soft Lithography Using Composite Stamps. *Langmuir.* 2002; 18:5314–5320.
23. Bowden N, Brittain S, Evans AG, Hutchinson JW, Whitesides GM. Spontaneous Formation of Ordered Structures in Thin Films of Metals Supported on an Elastomeric Polymer. *Nature.* 1998; 393:146–149.
24. Genzer J, Groenewold J. Soft Matter with Hard Skin: From Skin Wrinkles to Templating and Material Characterization. *Soft Matter.* 2006; 2:310–323.

25. Imburgia MJ, Crosby AJ. Rolling Wrinkles on Elastic Substrates. *Extreme Mechanics Letters*. 2016; 6:23–30.
26. Ebata Y, Croll AB, Crosby AJ. Wrinkling and Strain Localizations in Polymer Thin Films. *Soft Matter*. 2012; 8:9086–9091.
27. Khang D-Y, Rogers JA, Lee HH. Mechanical Buckling: Mechanics, Metrology, and Stretchable Electronics. *Adv. Funct. Mater.* 2009; 19:1526–1536.
28. Nania M, Matar OK, Cabral JT. Frontal vitrification of PDMS Using Air Plasma and Consequences for Surface Wrinkling. *Soft Matter*. 2015; 11:3067–3075. [PubMed: 25742777]
29. Liao X, Braunschweig AB, Mirkin CA. "Force-Feedback" Leveling of Massively Parallel Arrays in Polymer Pen Lithography. *Nano Lett.* 2010; 10:1335–1340. [PubMed: 20184292]
30. Zheng Z, Daniel WL, Giam LR, Huo F, Senesi AJ, Zheng G, Mirkin CA. Multiplexed Protein Arrays Enabled by Polymer Pen Lithography: Addressing the Inking Challenge. *Angew. Chem., Int. Ed.* 2009; 48:7626–7629.
31. Basabe-Desmonts L, Reinhoudt DN, Crego-Calama M. Combinatorial Fabrication of Fluorescent Patterns with Metal Ions Using Soft Lithography. *Adv. Mater.* 2006; 18:1028–1032.
32. Wang Y, Giam LR, Park M, Lenhart S, Fuchs H, Mirkin CA. A Self-Correcting Inking Strategy for Cantilever Arrays Addressed by an Inkjet Printer and Used for Dip-Pen Nanolithography. *Small*. 2008; 4:1666–1670. [PubMed: 18654990]
33. Zhong J, Sun G, He D. Classic, Liquid, and Matrix-Assisted Dip-Pen Nanolithography for Materials Research. *Nanoscale*. 2014; 6:12217–12228. [PubMed: 25251309]
34. Eichelsdoerfer DJ, Brown KA, Mirkin CA. Capillary Bridge Rupture in Dip-Pen Nanolithography. *Soft Matter*. 2014; 10:5603–5608. [PubMed: 24965488]
35. Chai J, Huo F, Zheng Z, Giam LR, Shim W, Mirkin CA. Scanning Probe Block Copolymer Lithography. *Proc. Natl. Acad. Sci. U. S. A.* 2010; 107:20202–20206. [PubMed: 21059942]
36. Chai J, Wong LS, Giam L, Mirkin CA. Single-Molecule Protein Arrays Enabled by Scanning Probe Block Copolymer Lithography. *Proc. Natl. Acad. Sci. U. S. A.* 2011; 108:19521–19525. [PubMed: 22106270]
37. Liu G, Eichelsdoerfer D, Rasin B, Zhou Y, Brown KA, Liao X, Mirkin CA. Delineating the Pathways for the Site-Directed Synthesis of Individual Nanoparticles on Surfaces. *Proc. Natl. Acad. Sci. U. S. A.* 2013; 110:887–891. [PubMed: 23277538]
38. Chen PC, Liu G, Zhou Y, Brown KA, Chernyak N, Hedrick JL, He S, Xie Z, Lin QY, Dravid VP, O'Neill-Slawecki SA, Mirkin CA. Tip-Directed Synthesis of Multimetallic Nanoparticles. *J. Am. Chem. Soc.* 2015; 137:9167–9173. [PubMed: 26144242]
39. Nie Z, Kumacheva E. Patterning Surfaces With Functional Polymers. *Nat. Mater.* 2008; 7:277–290. [PubMed: 18354414]

Figure 1.

(a) Wrinkle wavelength as a function of silica thickness; (b) silica thickness as a function of deposition time (slope 0.55 ± 0.03 nm/s); (c) bright-field image of silica deposited onto a slab of PDMS, 200 μm scale bar; (d) dark-field image of hard transparent array when it is at the goldilocks thickness of 175 nm, 50 μm scale bar; (e) dark-field image of shattered hard transparent array tips after patterning rhodamine 6G when silica thickness is too thin at 83 nm, 50 μm scale bar; (f) bright-field image of hard transparent array when silica thickness is too large, here 250 nm; buckling goes through the tips, 100 μm scale bar.

Figure 2.

Patterning MHA using (a) a hard transparent array and (b) a polymer array, both with an extension sweep covering 5 μm piezo range with 1.5 $\mu\text{m/s}$ extension and withdraw speed and no dwell time at full extension; patterning MHA using (c) a hard transparent array and (d) a polymer array, both with an extension sweep over 5 μm piezo range with 100 $\mu\text{m/s}$ extension and withdraw speed and 5 s dwell time. All scale bars are 2.5 μm . The white arrows indicate the direction of patterning. Images were taken using lateral force microscopy using AFM.

Figure 3.

Patterning polymer ink with an (a) extension sweep over 5 μm piezo range with 100 $\mu\text{m/s}$ extension and withdraw speed using hard transparent arrays and a dwell time of 2.5 s at full extension; (b) hard transparent arrays extension sweep over 4.2 μm piezo range with 3 $\mu\text{m/s}$ extension and withdraw with no dwell time at full extension; and (c) PPL extension sweep over 5 μm piezo range with the left half corresponding to the conditions in image a and the right half corresponding to image b. Scale bars are 2.5 μm . The white arrows indicate the direction of patterning. Images were taken with AFM in tapping mode.

Figure 4.

(a) AFM of a dot array with a 175 nm pitch in a hexagonal pattern array written using hard transparent array, 200 nm scale bar; (b) single polymer feature with a circle of small droplets from original meniscus, 20 nm scale bar; (c) dark-field optical microscopy of array with 500 nm pitch written using hard transparent array with PPL with 14 641 features written per pen, 100 μm scale bar; and (d) zoomed in image pattern made from a single pyramidal pen, 25 μm scale bar.

Scheme 1.
Fabrication process for hard transparent polymer pen arrays.