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Serial and Parallel Dip-Pen Nanolithography Using a Colloidal Probe Tip

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Dip-pen nanolithography (DPN)[1] has become a versatile and widely used lithographic technique. This patterning methodology requires direct contact between the "pen" (atomic force microscope (AFM) tip) and substrate. Many substrates including inorganics[2] and tissues[3] can be modified with various inks using this approach. One can apply the technique in both passive and active[4] parallel modes. Numerous examples have been reported in the literature to expand the versatility of the method. Relatively few reports have been published that utilize soft tips without the need for additional fabrication. Here we report the development of a passive, parallel DPN methodology that takes advantage of the attributes of a polymer colloid at the end of the AFM tip. The approach takes advantage of the chemical properties of the colloid on the tip (ability to swell under different environmental conditions) rather than relying on microfabrication advances that enable the production of arrays of "writing" pens.

AFM probes with specialized polymer coats[5] and tips[2,6,7] were previously reported to produce patterns. Notably the DPN stamp tip used a polydimethylsiloxane (PDMS) coating on a standard tip for stable patterning of lines and dots. In this report, we utilize a colloid terminated cantilever based off of methods others have employed for mechanical sensing as well as an understanding of substrate−tip force interactions.[5] We chose to utilize a colloid at the end of an AFM tip because humidity sensing approaches have relied on producing inexpensive thin films with such colloids for testing under variable humidity conditions.[8] A schematic of the strategy to make contact with the surface using a single tip or an array of tips is shown in Figure 1A. The colloids for all experiments were made from poly(methyl methacrylate) (PMMA), because they are commercially available and easy to attach onto the tip and their swelling behavior is affected by water as well as pH conditions.[9] To perform the proof-of-concept experiments with the single cantilever, the colloid terminated tip approached the surface and retracted, and then the humidity was increased. An increase in humidity causes the PMMA colloid to swell and enables it to make contact with the surface. It is important to note that the capillary force under increased humidity conditions can also cause bending of the colloidal probe tip. The same steps were followed when an array of tips was validated where one tip was used for laser alignment. The reported approach is an alternative to the polymer pen reported earlier.[7] It does not provide advantages in resolution but can be used to do alignment on soft surfaces, and if one utilizes colloids with variable swelling behavior[10] on each cantilever it can be possible to actuate them one at a time by simply changing the environmental conditions to tune their chemical behavior.

Patterning was carried out on different surfaces using the microsphere terminated tips.[11] ∼5 μm PMMA microsphere tips (k = 0.05 N/m, Novascan Technologies, Ames, IA) were used to pattern on gold surfaces (SPI Supplies, West Chester, PA), SiO_x surfaces, and SiO_x modified with two layers of polyelectrolytes, poly(allylamine hydrochloride) and poly(styrene sulfonate) (see Supporting Information for experimental details and additional data). The ink solutions were composed of 16-mercaptohexadecanoic acid (MHA), 1-octadecanethiol (ODT), laminin purchased from Sigma, (St. Louis, MO), and a collagen binding peptide previously used for DPN.[3] The tips were prepared by dipping in the ink for at least 30 min followed by air drying. All patterning and imaging were carried out using a Multimode IIIa SPM (Veeco Instruments, Santa Barbara, CA) with controllable humidity via a home-built chamber around the microscope. Initially, we tested the methodology using a single tip with the different inks, using an applied load of ∼150 nN.

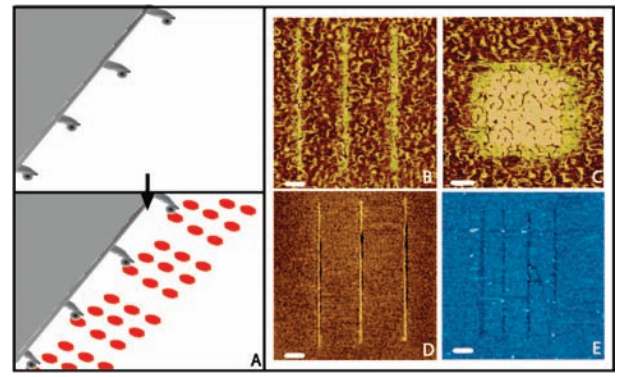

Figure 1. (A) Schematic of the DPN process using a colloidal probe tip in parallel mode. Multiple patterns can be produced with this technique. Representative lateral force microscopy (LFM) images of patterns produced in a serial mode: (B) lines of MHA on gold; (C) dot of MHA on gold; (D) line of peptide on clean SiO_x, and (E) lines of laminin on SiO_x modified with two layers of polyelectrolytes. All scale bars are 1 μm.

Several standard tests were performed to verify that the single colloid tip is producing typical DPN patterning, Figure 1B and C. Different shapes of patterns were tested with the thiol inks. The results compare very well with the previously published patterning of thiols.[12] By changing the tip speed one can vary the width of the lines, and by adjusting the dwell time the diameter of dots can be modulated. High resolution AFM imaging demonstrated that we formed good quality self-assembled monolayers similar to prior publications.[13] We assured that the patterns are not simply physisorbed on the surface by washing the features with ethanol and carrying out a successful reimaging of the same patterns. The same types of patterning tests were also done on clean SiO_x surfaces with peptide ink, Figure 1D, and on "soft" SiO_x modified with polyelectrolytes, using laminin as an ink, Figure 1E.

Others have recognized and reviewed the benefits of advancing DPN to a massively parallel technique.[14,15] We performed several studies to demonstrate that cantilevers terminated on colloidal probes can be used in a parallel fashion without any additional equipment or instrument modification. Parallel probes (8 cantilevers, k = 0.03 N/m, Nanoworld, Neuchâtel, Switzerland) were purchased,

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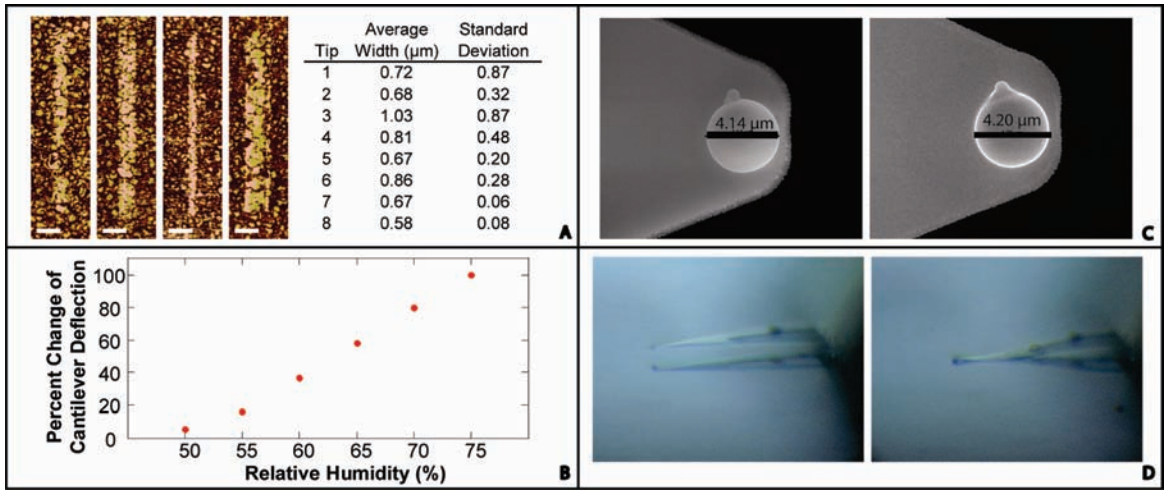

Figure 2. Parallel DPN using a colloidal probe tip A) representative LFM images after patterning with MHA, scale bar 1 μm; B) One can track the percent change in cantilever bending as a result of increase in relative humidity; C) E-SEM images of before (left) and after (right) an increase in humidity; D) digital photographs showing the cantilever terminated on a PMMA colloid before (left) and after (right) increase in humidity. The second cantilever on each image is a reflection of the tip on the substrate.

and microsphere attachment was performed by Novascan (Ames, IA). We demonstrated that all eight tips can write thiols on the surface simultaneously using our approach and an applied load of ~230 nN. Representative results are summarized in Figure 2A. We note that not all spheres were the same size; one can significantly improve the results if the type and size of the colloids are improved. Others have documented how humidity affects the size of the meniscus and thusly ink transportation rates to the substrate.[16] Upon increasing the humidity, one expects colloid swelling to produce both an increased size and mass. In fact one can monitor the changes in tip bending of individual tips as the humidity is gradually changed, Figure 2B. The effect of increased humidity on the PMMA microsphere tips is evident in environmental scanning electron microscopy (E-SEM) using an approach described by Weeks et al. to monitor the formation of the meniscus during the DPN process.[17] The setup in the E-SEM does not permit easy imaging of all tips swelling, but one can examine them one at a time and verify their presence after multiple writings. During E-SEM studies tip expansion can be observed when the relative humidity is increased from 30−100% (Figure 2C). The colloidal tip approach we report relies on the fact that one can facilitate easier contact of all probes through cantilever bending and increasing the microsphere contact surface area. We have used a digital camera to record how the tip observably bends when left above the surface after an increase in humidity, Figure 2D. One does not need to use any kind of alignment procedure to bring the tips in contact with a desired substrate.

This new procedure for DPN has great potential. First, the microsphere probes are stable during active patterning. They readily pattern multiple structures, under variable conditions, with different inks. After 1 h of contact time the tips could still produce similar patterns after reinking. Second, the swelling of the tip(s) can be controlled in any chamber with the capability of adjusting the humidity conditions and the resultant bending of the cantilever can be observed right away. We note that humidity does affect the patterning results with many inks. The resolution that one achieves is dependent upon the chosen surface and the ink being delivered. The reason for electing to pattern with a colloidal tip is not to achieve high resolution but to preserve the substrate being modified and place specific molecules on rough and soft surfaces, such as tissues. For this particular application one does not need to produce small lithographic patterns. The DPN procedure with a colloidal probe allows one to do site specific placement, utilize multiple inks, and avoid mechanical damage to soft surfaces.

Supporting Information Available: Additional data and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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