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Transport Rates Vary with Deposition Time in Dip-Pen Nanolithography

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By patterning with dip-pen nanolithography using tip dwell times ranging from 15 s to 2 h over a period of 19 h, we show that the transport rate for smaller patterns is different than for larger ones. This transport behavior is found for both 1-octadecanethiol (ODT) and 16-mercaptohexadecanoic acid (MHDA) inks on gold substrates. Additionally, MHDA shows an overall decrease in transport rate as a function of total writing time during such experiments. These results indicate that measurements with short dwell times are insufficient to determine transport rates for larger features.

After the first observation of the transport of material from an atomic force microscope (AFM) tip to a substrate by Jaschke and Butt in 1995,[1] Mirkin and co-workers developed the method into the patterning technique known as dip-pen nanolithography (DPN).[2,3] The first DPN experiments used alkanethiols as an "ink" and gold substrates.[3] The technique has since been extended to a wide variety of ink−substrate combinations, including polymers, biological molecules, colloidal particles on semiconductor oxides, and noble metals,[2] and a range of applications from lithographic resists [4−6] to biologically compatible surfaces.[7−9] Despite the interest in DPN as a versatile patterning tool, the transport mechanism of the ink from the tip to the surface, for even the simplest systems, remains under debate; studies of ink transport in DPN remain lacking, despite the critical impact of this on feature size.

The transport rate of the molecular ink depends sensitively on both the environmental conditions and the exact nature of the inked cantilever and the substrate surface. Therefore, the first step in any patterning with DPN is measurements of the molecular transport rate of the ink by patterning dots with varying dwell times or lines with varying tip speeds. Assuming a constant flux of molecules from the molecularly coated cantilever to the surface, the patterned area will be proportional to the dwell time. The assumption of a constant transport rate generally has been found to be valid; however, the rate constant can vary significantly from experiment to experiment.[10−14]

Until now, the stationary tip measurements reported in the literature have had dwell times ranging from a few seconds to a few minutes.[11,13−16] However, the transport rate measured with these short dwell times may not be valid when extrapolated to longer dwell times if patterns with large size scale (such as those relevant to bioanalytical applications) are desired. In particular, the assumption of a constant transport rate does not take into account any effects of the already-deposited ink on the transport of subsequent ink. Small changes in the molecular transport rate as a result of the previously patterned ink would not be evident in short time calibration measurements. Here, we present results from extended time measurements of the two most common ink−substrate combinations used in DPN, 16-mercaptohexadecanoic acid (MHDA) and 1-octadecanethiol (ODT) on Au surfaces, and show that the dwell time does indeed affect the transport rate.

Detailed experimental procedures are given in the Supporting Information. Briefly, the DPN patterning was performed using a ThermoMicroscopes Autoprobe CP Research AFM in an inert environment at a relative humidity of 21 ± 1% and temperature of 24 ± 1 °C. The AFM was operated in contact mode using silicon-nitride-coated plank-style cantilevers with force constants of 0.05 N/m. Cantilevers were inked with ODT by vapor deposition. Cantilevers inked with MHDA were prepared following the "double dipping" procedure from a 5 mM acetonitrile solution of MHDA.[17] Both ODT and MHDA were patterned on Au{111} on mica substrates using the Nanolithography module in the ProScan software package. The DPN-generated structures were imaged in lateral force microscopy (LFM) mode using un-inked cantilevers.

Long-time measurements were performed for ODT and MHDA by writing a set of 11 dots with dwell times ranging from 15 s to 2 h. The use of dot features allowed us to determine the ink transport rate without the added influence of the tip velocity that would be present if line features were used. In each case, the set of 11 dots was repeated two additional times, resulting in three copies of the set of dots in a total writing time of 19 h. For the first set of dots, the dot dwell times started at 15 s and increased to 2 h, while for the final two sets, the dwell times were reversed and started with 2 h and decreased to 15 s. By reversing the order of the dot dwell times for Sets 2 and 3, the writing behavior could be broken down into two independent contributions, a dependence on the total writing time and a dependence on the dot dwell time.

The areas of each of the 33 patterned dots were calculated from LFM images (see Supporting Information), and the transport rate for each dot was determined by dividing the dot area by the corresponding dot dwell time.

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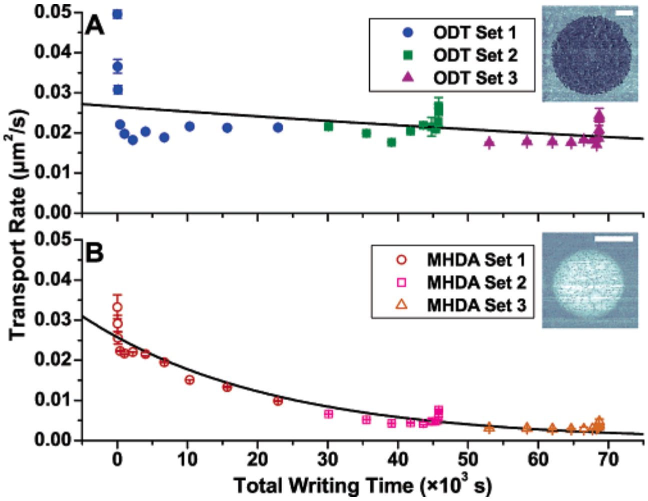

Figure 1. Transport rate (dot area divided by dot dwell time) as a function of the total writing time for extended time calibrations with ODT (A) and MHDA (B), and exponential fits (black lines) for each curve (see text for details). The insets show LFM images of (A) an ODT dot patterned with a dwell time of 1 h (11 μm × 11 μm, scalebar 2 μm, scan rate 4 Hz, force setpoint 1 nN) and (B) an MHDA dot patterned with a dwell time of 1 h (5 μm × 5 μm, scalebar 2 μm, scan rate 4 Hz, force setpoint 1 nN).

Figure 1 shows the results of these long calibration experiments, plotted as the molecular transport rate for both ODT (A) and MHDA (B) as a function of the total writing time (the length of time from the beginning of the experiment when the particular dot was written). For ODT, the transport rate is nearly constant except for sharp increases around 0 s, 46 × 10^3 s (∼12.8 h), and 69 × 10^3 s (∼19.1 h) total writing time. These three times correspond to the beginning of Set 1 and the ends of Sets 2 and 3, when dots with short dwell times were being written. In the case of MHDA, the measured transport rate decreased significantly during the course of the entire experiment. In addition to this overall decrease, similar to the results for ODT, the transport rate for MHDA increased at the beginning of Set 1 and the ends of Sets 2 and 3, when the dots with short dwell times were being patterned.

Consistent with the results shown in Figure 1A, Sheehan and Whitman observed no significant change in the transport rate of ODT throughout 24 h of continuous writing in a dry nitrogen atmosphere.[13] In contrast, Schwartz and co-workers reported decreases in MHDA transport rate over several hours of writing,[15] similar to Figure 1B. They observed roughly exponential decreases in the molecular transport rates with relaxation times ranging from tens of minutes to a few hours for cantilevers with various inking protocols. They attributed this phenomenon to depletion of the ink from the region of the cantilever near the surface as a result of extended periods of writing. In addition, solution-deposited cantilevers tended to have longer equilibration times and higher steady-state transport rates than those deposited by solutionless methods, indicating that solvent plays a critical role in determining the mobility and distribution of ink on (and from) the cantilever.

The data in Figure 1 for both ODT and MHDA were fit to exponential curves. As seen in Figure 1A, the exponential fit does not fit the ODT data ($R^2 = 0.18$). However, for MHDA (Figure 1B), the exponential curve agrees reasonably with the data, except at the beginning of Set 1 and the ends of Sets 2 and 3 (these data were included in the fit), when the dots with short dwell times were patterned ($R^2 = 0.94$). The observed relaxation time ($1/k$ from $A\exp(-kt)$) of 7.5 ± 1.0 h is longer than that reported by Schwartz and co-workers. The different

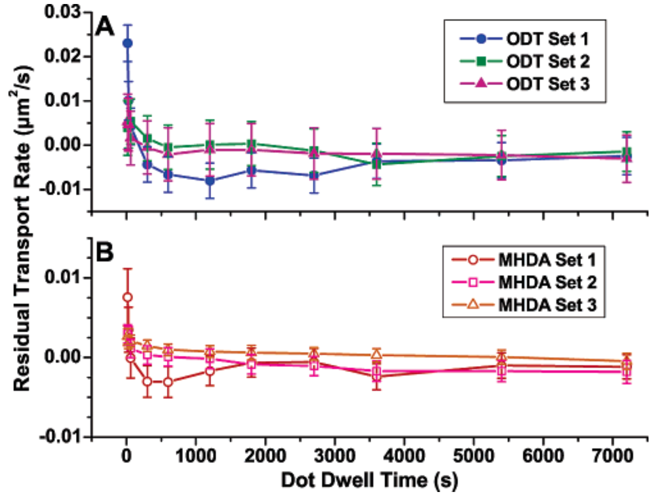

Figure 2. Residual transport rate (measured transport rate − exponential fit) as a function of dot dwell time for ODT (A) and MHDA (B).

inking protocols used as well as the variability from tip to tip observed by Schwartz even for nominally identical inking protocols[12] offer an explanation for this difference.

The ink transport as a function of dwell time can be observed from the residual transport rate (measured transport rate − fit). Figure 2 shows these residual transport rates for both ODT (A) and MHDA (B) plotted as a function of the dot dwell time for each set of dots. When corrected for the overall trend with writing time and plotted as a function of dot dwell time instead of total writing time, the data for each set of dots are consistent, and the trends in transport rate with dot size are clear. For both ODT (Figure 2A) and MHDA (Figure 2B), the residual transport rate was highest for small dot dwell times and decreased to a relatively constant value for dwell times greater than 300 s.

This behavior highlights the fact that patterning small features (i.e., short dwell times) gives different results than patterning large features (long dwell times). In particular, the transport rate for small dwell times, when the inked cantilever writes on an unpatterned substrate, is higher. For longer dwell times, when the cantilever continues to pattern a region that already has ink patterned on it, the transport rate is lower. Thus, short-time measurements are inaccurate in determining the transport rates for features patterned with longer dwell times. To ensure that large DPN features have the desired sizes, pre-patterning transport rate measurements need to be on the same time scale (and thus size scale) as those features.

For all the extended time studies performed in our laboratory, we observed both overall decreases in the MHDA transport rate with writing time and that the writing for small dwell times differed from those for long dwell times. However, quantitatively, the writing showed large variability from experiment to experiment.

The extended time results presented here demonstrate that the transport of thiol inks such as MHDA and ODT can be affected significantly by the state of the substrate. The presence of ink already on the surface can slow the transport rate for additional ink. A further consequence of this observation is that the exact nature of the substrate used for a particular DPN experiment can affect the behavior of the ink during patterning. Any adsorbates on the patterning substrate (whether placed there intentionally by earlier patterning steps or present unintentionally due to insufficient cleaning or ambient contamination) can affect the ink transport rate or even cause the patterning to fail. Uncontrolled surface chemistry may be the source of much of the variation found in the literature for dip-pen nanolithography of thiol inks on gold surfaces.[10−14]

Both the intrinsic characteristics (such as hydrophobicity) of a particular ink molecule and the interactions of the molecules with residual solvent are expected to influence the transport rate of the ink when patterning on top of an existing monolayer. Further experiments are ongoing in our laboratory to quantify the effects of different surface adsorbates on ink transport during dip-pen nanolithography.

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Supporting Information Available: Detailed experimental and analysis procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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