

Colored ink dip-pen nanolithography

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Colored ink dip-pen nanolithography (DPN) is demonstrated by the direct patterning of organic dyes on substrates to generate optically active and arbitrarily shaped nanostructures with dimensions well below 200 nm in a straightforward manner. The dye nanopatterns are indeed optically active as confirmed by fluorescence emission under external pumping. The efficiency of patterning organic materials on bare and chemically modified Si/SiO_x substrates reaffirms that DPN patterning of organic molecules can be done without covalent linkages, and points to importance of noncovalent interactions in DPN. The method can be extended to direct patterning of many colored/colorless organic molecules, and should open many opportunities for miniaturized optical devices and site-specific biological staining. © 2002 American Institute of Physics.

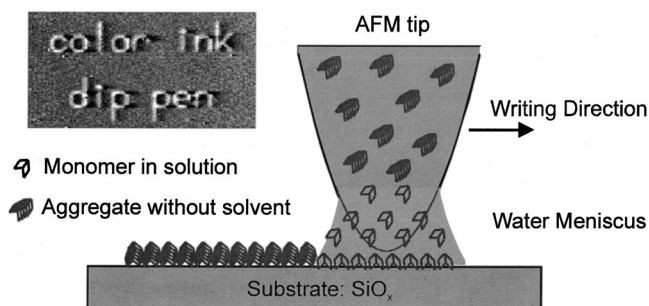
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Arbitrarily controlled patterning of functional molecules at nanometer scale is a critical step to construct miniaturized devices. Intense efforts have been focused on the development of nanometer scale approaches analogous to macroscopic tools.^{1–6} Dip-pen nanolithography (DPN), in which inks adsorbed on the tip of atomic force microscope (AFM) are transported to a flat substrate via capillary force, can generate two-dimensional nanostructures of arbitrary shapes with dimension on sub-100 nm length scales.⁷ The initial DPN was demonstrated by patterning thiol-functionalized organic molecules on gold surfaces through the water meniscus formed between the tip and the substrate. These nanopatterns can be used as templates to construct highly ordered nanoarrays of smaller building blocks.^{8,9} A great advantage of DPN is the site-specific patterning of multiple inks at the same location with high registry.¹⁰ However, this advantage is not as pronounced if the subsequent steps need parallel operations such as dipping into other solutions to form patterns. Thus, it is highly desirable if the required molecules can be directly patterned without additional steps. In principle, DPN can be extended to the direct patterning of nearly any soluble materials onto almost all flat substrates. Experimentally, the numbers of inks that can be directly patterned are limited to several types of materials that can form covalent bonding with the substrates, which include, for example, thiol-functionalized protein and deoxyribonucleic acid (DNA) on a gold substrate, silanes on semiconductor substrates, metal nanostructures on conductive surface, and some sol-gel composite inks on many substrates.^{11–14}

Here, we demonstrate the concept of “colored” ink DPN by the direct patterning of four representative organic dyes on bare or chemically modified Si/SiO_x substrates. The idea of using dye inks comes from the fluorescence staining of biological materials and the dyeing of organic fibers in textile industry, where ionic dyes bind with fiber, polyelectrolytes, proteins or DNA that have ionized groups through

various noncovalent interactions. Principally, these organic dyes have similar physical and chemical properties with colorless organic molecules except for their illumination characters, thus other colorless organic molecules, could also be readily patterned by DPN.

Scheme 1 shows several key steps of colored ink DPN:



(1) The formation of randomly distributed aggregates on an ink-coated tip after solvent has evaporated; (2) The disassembly of larger aggregates to individual molecules or smaller aggregates inside the water meniscus; (3) the diffusion of dye molecules from the tip to the substrate; (4) the attachment of the dye molecules by noncovalent attractions with the substrates; and (5) the subsequent aggregation of dyes upon solvent evaporation. As proof-of-concept experiments, rhodamine 6G (R6G), coumarin 6 (C6), acid red 8 (AR8) and fluorescein (FITC) were patterned on silicon oxide or modified silicon substrates.

All patterning and imaging experiments were done under an ambient condition at relative humidity of ~30% and temperature of ~23 °C using a ThermoMicroscopes CP AFM driven by customized software. Conventional Si₃N₄ cantilevers (ThermoMicroscopes sharpened microlever A, force constant of 0.05 N/m) were used in all the experiments. Subsequent imaging of the generated patterns was performed with the ink-coated tip under conditions identical to those for patterning but at a higher scan rate (4 Hz).

Silicon (100) wafers with thick oxide layer (>600 nm) were used after a thorough cleaning in sonication baths of

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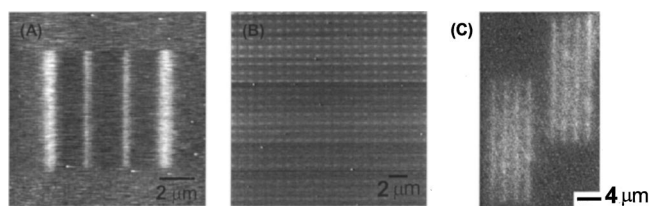


FIG. 1. (a) Topographic AFM image of R6G patterned on Si/SiO_x substrate; the writing speeds for each line (from left- to right-hand side) are 0.05 μm/s, 0.2 μm/s, 0.2 μm/s, and 0.05 μm/s, respectively. (b) Dots array of R6G formed by successively holding an R6G-coated tip on the substrate. The holding time for each dot is 1 s. (c) Fluorescence microscope image of 20 μm parallel lines formed by moving an R6G-coated tip at a tip moving speed of 0.1 μm/s.

water and alcohol, respectively. The substrates are negatively charged in water due to the existence of exposed hydroxyl groups. The dyes studied here were obtained from Aldrich and used without further purification. Prior to the DPN patterning experiment, AFM tips were dipped into a 0.05 mM dye solution in water (R6G and AR8) or in ethanol (C6 and FITC) for about 20 s and blown dry with compressed difluoroethane. Fluorescence images were collected on a Zeiss Axiovert 100A fluorescence microscope.

R6G shows strong fluorescence and has been widely used as laser dye. The cationic dye can be easily patterned on negatively charged Si/SiO_x substrate. Four parallel lines are formed by scanning a Rh6G-coated tip across an arbitrarily selected area on the substrate. Immediately after the deposition, a topographic AFM image within a larger scan area allows one to distinguish the pattern from the surrounding substrate [Fig. 1(a)]. The widths of these lines were controlled by moving the ink-coated tip at the speed of 0.05, 0.02, 0.2 and 0.05 μm/s (from the left- to right-hand side). The topographic feature (height range from 0.8 to 3 nm) is higher than the length of the molecule (less than 1 nm). This suggests the formation of aggregates of the dyes upon the evaporation of solvent. The patterned structures also exhibit relatively higher lateral force that means the dye molecule has strong interaction with the substrate. Figure 1(b) shows the image of a high-density dots array formed by holding the R6G-coated tip on the substrate. The holding time for each dot is 1 s. More complex features as that shown in Scheme 1 (inset) can be formed easily by driving the R6G-coated tip across a predetermined pathway. These patterned nanostructures are stable in air for more than one week, which exclude the possibility of any solvent condensation.

Figure 1(c) shows the fluorescence emission from eight parallel lines (length of 20 μm), which were patterned on Si/SiO_x substrate at the tip moving speed of 0.1 μm/s. The fluorescence image was collected in reflect mode when illu-

minated by 488 nm pumping light. The uniform photoillumination indicates that the dye molecules are uniformly distributed within the pattern.

Using the similar procedure, we have patterned C6, FITC, and AR8 on bare or chemically modified Si/SiO_x substrates by DPN. Among these, C6 is a neutral organic dye and FITC and AR8 are anionic organic dyes. We found diffusion of C6 very fast on Si/SiO_x substrate during DPN patterning, although there seems no electrostatic interaction between C6 with the substrate. The anionic FITC and AR8 are negative charged in water solutions; they are supposed to be negatively charged in the tiny water meniscus formed between the AFM tip and the substrate. For their patterning, we prepared chemically modified substrates by dipping the bare Si/SiO_x substrate into 1 mM solution of 3-aminopropyltrimethoxysilane in ethanol for 30 min. The modified substrate is positively charged in water and also has strong ability to form hydrogen bond due to the existence of amine groups. FITC and AR8 can be easily patterned on the chemically modified substrate. In addition, we tried to pattern FITC and AR8 on bare Si/SiO_x substrate. It is surprising that the two negative charged dyes could be patterned on the negative charged substrates, reaffirming that noncovalent interactions may also play an important role in the DPN.

In principle, at least four types of noncovalent interaction exist between dye molecules and substrates, namely electrostatic force, van der Waals' force, hydrophobic interaction, and hydrogen bonding.¹⁵ In reality, organic dyes interact with their substrates in a complex way and it is difficult at this time to differentiate experimentally which one has a predominant effect. On the other hand, although complex, the interaction between the dyes and the substrate is strong enough to withstand the imaging force from AFM tip. Actually, the imaging force can be controlled small enough to observe the nanostructures of water patterned by the similar DPN process.¹⁶

The diameters of dots formed by R6G and C6 increase with longer tip-substrate contact times [Fig. 2(a)]. The data for octadecanethiol (ODT) on gold substrate are shown in Fig. 2(a) for comparison. The widths of lines formed by FITC and AR8 reduce at higher tip moving speed [Fig. 2(b)]. The expected $t^{1/2}$ dependence of dot diameter is in accord with the model used to describe DPN process.^{17,18} The large difference in the dimensions of patterned structures can be attributed to the structural difference of the four dyes. When the organic dyes are dissolved in the water meniscus, the physical properties of the water meniscus (e.g., mobility and surface tension) are certainly changed.

In conclusion, we demonstrate the ability of DPN to directly pattern organic dyes through the concept of colored

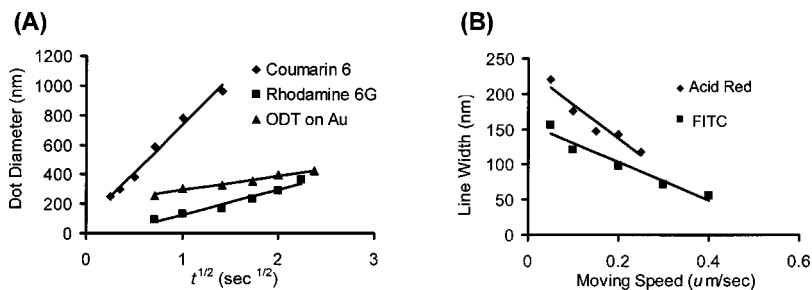


FIG. 2. (a) Plot of the diameters of dots as a function of $t^{1/2}$ for R6G and C6 on Si/SiO_x, and ODT on Au. (b) Plot of the line widths as a function of tip moving speed for FITC on bare Si/SiO_x and AR8 on amine-modified Si/SiO_x.

ink DPN. Three types of organic dye (anionic, cationic, and neutral) have been patterned on bare silicon surface or amine-modified substrate. The colored ink DPN approach may have potential applications in high-density optical information storage,¹⁹ miniaturized optical devices²⁰ and biological staining,²¹ among potentially many others. Combined with the recent progress in single molecular fluorescence and the highly localized ability of AFM, the molecular delivering of colored ink DPN enables site-specific staining of tissues, protein film and even individual cell, at the nanometer scale.

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