AFM Study of Water Meniscus Formation between an AFM Tip and NaCl Substrate

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Water meniscus formation at the point of contact between an AFM tip and an atomically smooth NaCl substrate was experimentally studied as a function of atmospheric water content, from 70% relative humidity to ultrahigh vacuum (UHV). Meniscus formation was probed by measuring the pull-off point and evaluating the ability of the meniscus to dissolve the NaCl near the point-of-contact as a function of atmospheric water content. Hydrophilic and hydrophobic tips were studied, and although a decrease in meniscus size was observed for the hydrophobic tips, all data are consistent with both types of tips resulting in the formation of a meniscus even at 0% relative humidity.

Introduction

When scanning probe microscopy (SPM)[1] is performed under ambient conditions, water, which is present in the air and on the substrates to be investigated, forms a meniscus between the probe tip and the sample surface.[2] In most SPM applications, the water reduces the resolution of the scanning probe technique, and researchers go to great lengths to minimize its effect.[3] However, in some SPM modes, such as lateral force microscopy (LFM),[4] the interaction force between the tip and the sample is measured as a function of the frictional force between the two surfaces, which is significantly influenced by the water in the capillary. An understanding of the capillary effect and nature of the water meniscus is essential to improve the resolution of SPMs, obtain accurate numerical simulations of interaction forces, and develop new SPM techniques for nanofabrication under ambient conditions.

Meniscus formation between the tip of an atomic force microscope and a liquid film on a flat substrate has been studied experimentally and theoretically,[5−8] and the experimental effect of water on the imaging process is well-understood.[3,6,8,9] The results of these studies are important for many SPM applications, in particular, dip-pen nanolithography (DPN).[10] DPN is a technique that uses a commercial atomic force microscope for generating patterns of chemical inks on surfaces in direct-write fashion with nanoscopic resolution. It exploits the meniscus, in many cases, as a media for transporting inks to surfaces. Patterns made of inorganic materials, small organic molecules, and large biological structures have been fabricated by DPN.[10−16]

The process of ink deposition is complicated and not universal for all molecules. Different molecules exhibit diffusion behavior with different dependencies on humidity, temperature, and solvent.[13,17−21] A critical issue pertaining to DPN involves the role of the water meniscus during the deposition of ink molecules from the tip to a surface. Some researchers propose that under non-UHV conditions the meniscus is central to the transport process and will always play a role (facilitating or inhibiting) in ink transport from tip to substrate,[17,20] while others have concluded that a meniscus is not involved in the transport of certain molecules.[18,19] One of the reasons for this dichotomy in points of view is that the researchers who have come to the latter conclusion focused their studies on a volatile ink 1-octadecanethiol (ODT) under conditions that they referred to as 0% relative humidity. With respect to nonvolatile molecules, especially biomacromolecules such as DNA and proteins, it has been shown that the meniscus and substantial humidity are required to pattern with them.[13]

The claim that a meniscus does not form at 0% relative humidity and is therefore not important in the DPN process has been a point of concern. It is known that it is very difficult to remove adlayers of water, especially from hydroscopic surfaces such as Au, without high-temperature UHV conditions. Indeed, synthetic chemists often flame-dry their glassware under vacuum to remove such residual water, and UHV surface scientists bake out their vacuum chambers prior to commencing experiments for the same reason. On the basis of empirical observations in our laboratory[17] and the theoretical work done by Schatz,[22] we hypothesized that even under low humidity conditions, water on the surface of the substrate and tip will collect at the point of contact to generate a meniscus. To test this hypothesis, we have designed a series of AFM experiments on a NaCl crystal to evaluate the conditions under which water collects at the point of contact. NaCl was chosen because it is atomically flat, easy to image by AFM, and will dissolve when water collects at the point-of-contact. This paper examines the issue of meniscus formation on atomically flat NaCl as a function of relative humidity, including ambient, 0% as defined by Sheehan and Whitman,[19] and ultrahigh vacuum conditions.

Experimental Procedures

The NaCl samples used in these studies were prepared from a commercially available sodium chloride substrate purchased from International Crystal Labs.[23] A small piece of the crystal was cleaved under ambient conditions to obtain an atomically

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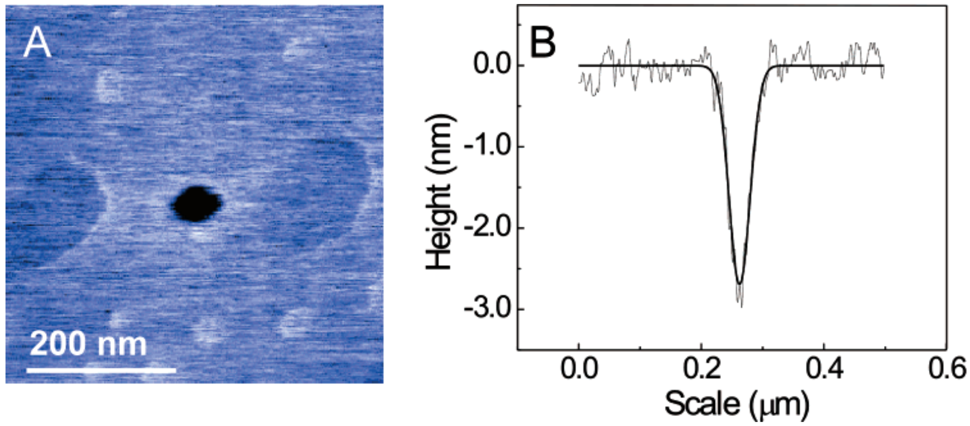


Figure 1. (A) AFM image of a pit formed on a NaCl surface after a bare tip was in contact (0.5 nN) with the surface for 1 min. The relative humidity was 40%. (B) The topography profile of the pit.

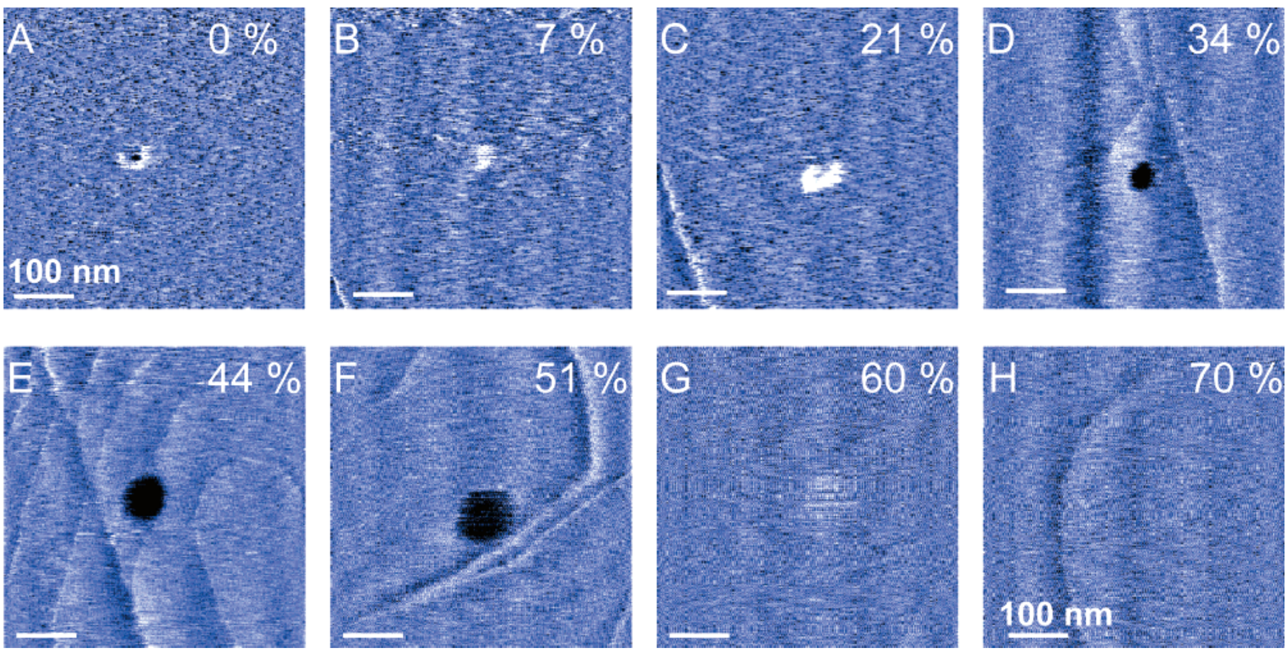
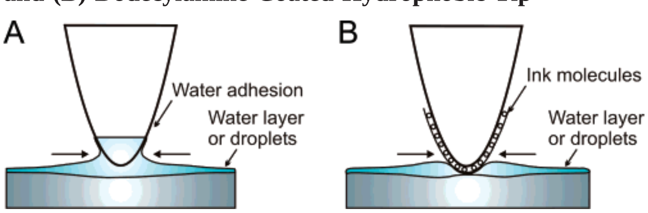


Figure 2. AFM images of pits formed at different humidities with a bare tip. The contact force was 1.0 nN, and the scale bar for all images is 100 nm.

SCHEME 1: Sketch of Water Meniscus Formation between NaCl Substrate and (A) Bare Hydrophilic Tip and (B) Dodecylamine Coated Hydrophobic Tip



flat surface. The roughness (rms) of the freshly cleaved substrate was less than 3 Å. The AFM tips were ultrasharp silicon nitride microlevers (model no. MSCT-AUHW, purchased from Veeco, Inc.;[24] spring constant, $k = 0.05$ N/m). Prior to use, the tips were washed in piranha solution (3:1 v/v; concentrated H_2SO_4/H_2O_2) for 30 min. (Caution: piranha is an aggressive and explosive chemical. Never mix piranha waste with solvents. Check the safety precautions before using it.) Because of piranha cleaning, the tip surface becomes hydrophilic,[25] which results in large capillary forces between the tip and the sample surface. Tips with hydrophobic surface properties were prepared by coating piranha-cleaned tips with dodecylamine[9] or octadecanethiol[10] (ODT) (purchased from Aldrich and used as received). These chemicals reduce water adsorption on the tip surface, which decreases the capillary effect.[9] The formation of a water meniscus between the AFM tip and the NaCl substrate was studied using a Thermomicroscope CP Research AFM[24] and UHV AFM from RHK Technology. In experiments carried out with the CP AFM, the system was enclosed in a small chamber (2.5 L), which covers the AFM head, and the humidity was controlled by introducing water vapor (bubbling N_2 through water) or dry nitrogen. With such arrangements, the relative humidity could be adjusted from 0 to 90% at a change rate of approximately 10% per hour. The humidity was monitored with a Fisher Scientific hygrometer with a lower limit of 0.01% sensitivity.[23] The experiments under UHV conditions were performed in a UHV chamber equipped with a scanning tunneling/atomic force microscope (RHK Technology) with a design similar to the one described by Besocke et al.[26,27] Pointprobes (n^+-silicon cantilevers, type Contr-W for contact-mode AFM; spring constant in the range 0.09−0.20 N/m; purchased from Nanosensors[28]) were used for all UHV measurements. The AFM was controlled using commercial electronics and software from RHK Technology, Inc. Prior to taking

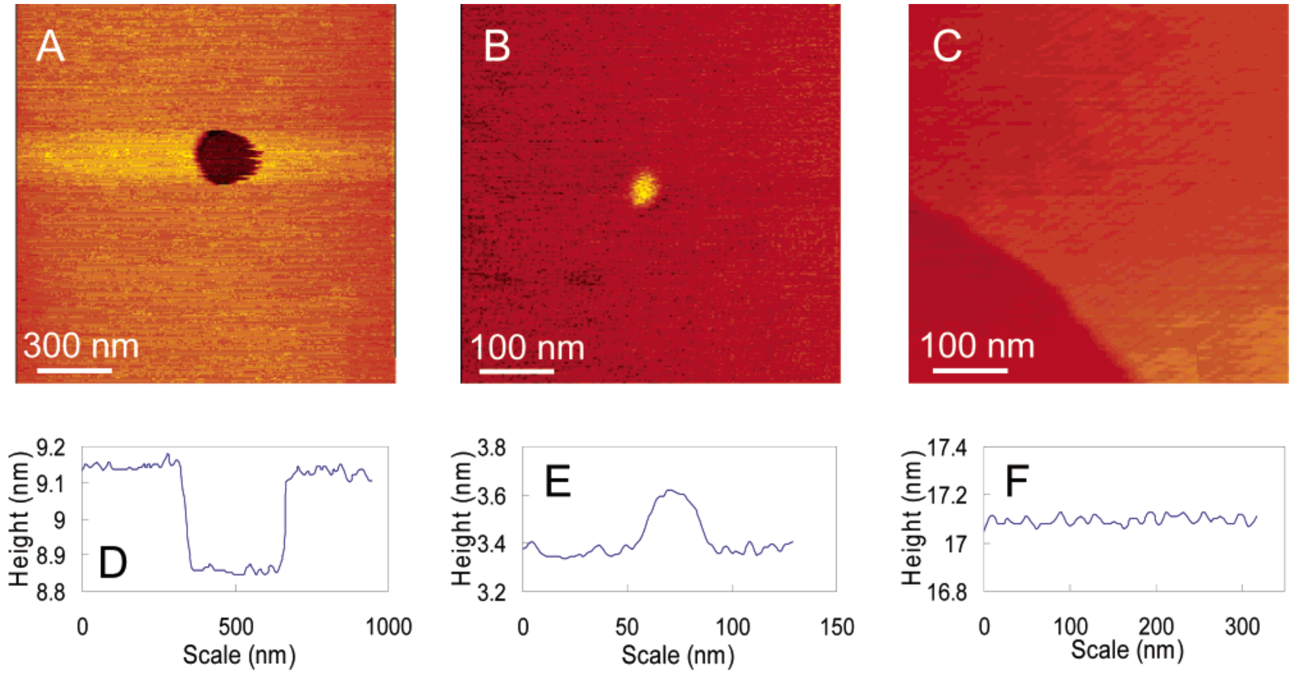


Figure 3. AFM images and topography profiles of features formed with a bare Si tip held in contact with a NaCl substrate for 1 min as a function of chamber water content. (A) Ambient, RH = 22%. (B) Dry N_2, RH = 0%. (C) UHV, 1.5 × 10^{-8} Torr. (D–F) Surface line scan across the point of contact.

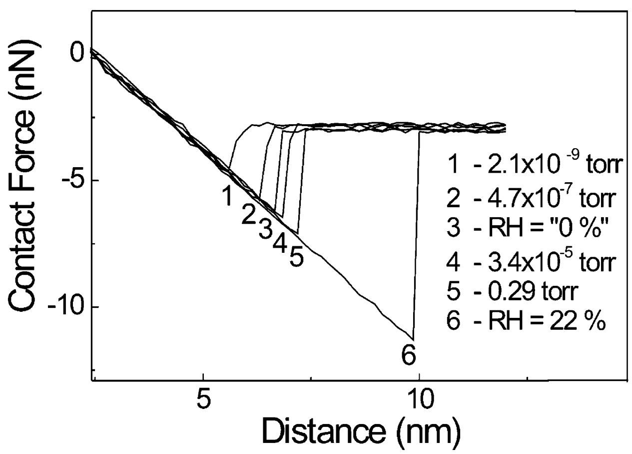


Figure 4. Force–distance curves measured as a function of chamber water content. (1) 2.1 × 10^{-9} Torr, (2) 4.7 × 10^{-7} Torr, (3) dry N_2, (4) 3.4 × 10^{-5} Torr, (5) 0.29 Torr, and (6) RH = 22%. The saturated vapor pressure of water under 1 atm and 21 °C is 18.650 Torr,[30] so the partial pressure of water at RH = 22% was calculated as 4.1 Torr (18.650 × 22%). The partial pressures of water in a vacuum (below 1 × 10^{-4} Torr) were calculated from the total pressure of the chamber, and the water percentage was measured using a residual gas analyzer. We estimate the partial pressure of water at the total pressure of 0.85 Torr by assuming that it is proportional to the total pressure with the same ratio as it is at the total pressure of 1 × 10^{-4} Torr. At 0.85 Torr, the partial pressure of water is approximately 0.29 Torr (0.85 × (3.4 × 10^{-5}/1 × 10^{-4})).

images and force–distance curves, the chamber was maintained at a specific pressure for several hours to allow equilibration of the water in the vapor phase and water adsorbed to the chamber walls, tip, and substrate. The total pressure in the UHV chamber was monitored using a vacuum gauge (Granville–Phillips 350), and a residual gas analyzer (Stanford Research Systems RGA 200) was used to measure the relative pressure of water and other residual gases at 1 × 10^{-4} Torr and below. At ambient pressure, the relative humidity was tested with a Fisher Scientific digital hygrometer inserted into the UHV chamber.[23] The 0% RH condition was achieved by flushing the chamber with dry nitrogen for 24 h.

Results and Discussion

To observe water solvating effects on NaCl, an AFM tip was held in contact (set point was 0.5 nN, relative humidity = 40%) with the surface for 1 min, and then the contact area was imaged with the same tip. An atomically smooth area on the substrate was chosen for these studies to minimize step-edge effects and the complication of data analysis. By placing the tip into contact with the substrate, capillary forces move the water on the tip and substrate surface to the point of contact, and a meniscus forms at the periphery of the tip, Scheme 1A. A small amount of NaCl dissolves in the meniscus, and a several nanometer (at least 3) deep pit appears on the surface under these conditions (Figure 1A). The hole may be deeper due to tip convolution in the imaging process.

Effect of Humidity on Pit Formation using a Hydrophilic Tip. Pit formation is significantly affected by changes in relative humidity (Figure 2A–H). In general, larger pits form at higher humidities, and smaller ones form at lower humidities. However, above 60% relative humidity, no pit formation is observed presumably because there is a saturation layer on the surface that makes the meniscus a continuum that extends across the surface and therefore minimizes localized NaCl dissolution. When the conditions of 0% humidity reported by Sheehan and Whitman were reproduced (dew point of −40 °C), pit formation was still observed, consistent with the collection of water at the point-of-contact, Figure 2A. The pit in this case as imaged by AFM is covered by recrystallized NaCl and appears as a raised feature in the image. These types of raised features were observed at 7 and 21% relative humidity (Figure 2B,C). At low humidity, a small dark spot, indicative of a lower feature, is occasionally observed at the center of the area of contact in the middle of the recrystallized area (Figure 2A). This is likely the direct point-of-contact between tip and sample where water has been minimized or excluded and dissolution has not taken place. Finally, if one conducts the same experiment with a UHV AFM,

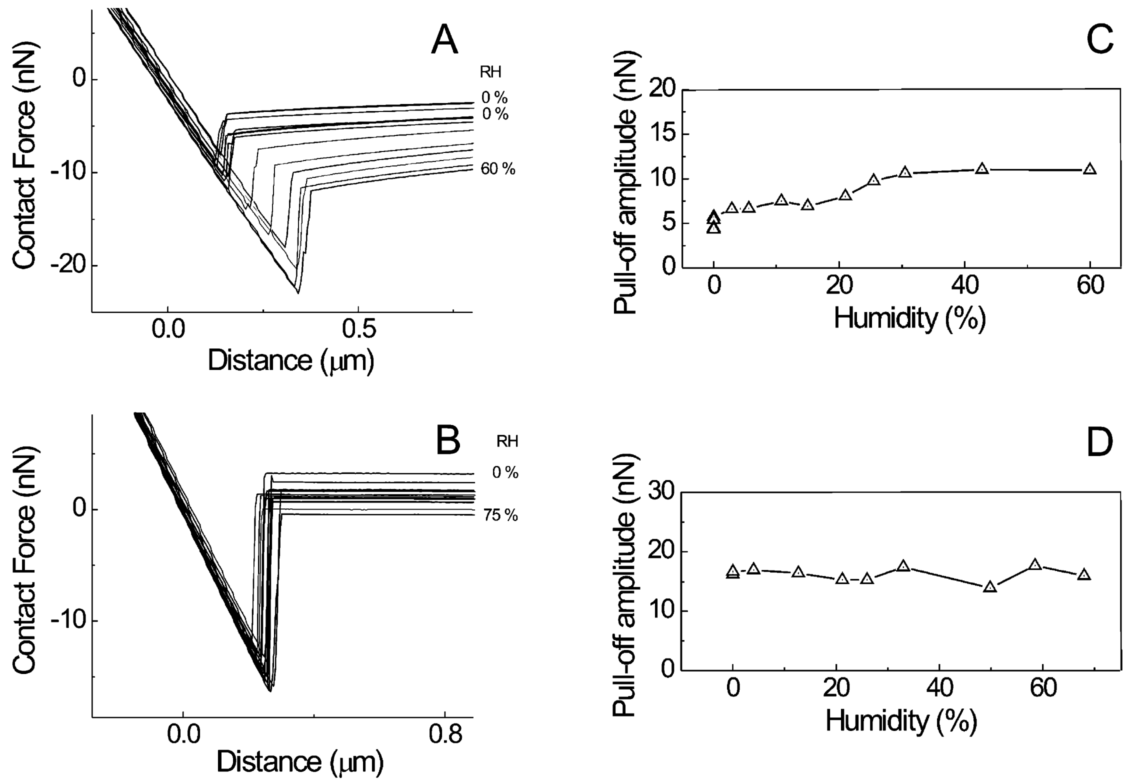


Figure 5. Force vs distance curves measured on NaCl as a function of humidity with (A) a hydrophilic and (C) hydrophobic tip. Panels B and D are relative plots showing changes in absolute values of pull-off amplitude as a function of humidity. Note that the absolute value of pull-off point varies from experiment to experiment for different tips or different instruments used. It is the relative values that are informative.

very similar results are observed, except pit formation is not seen under UHV conditions (1×10^{-8} Torr) (Figure 3). Relatively deep pits are observed at 22% RH, raised features are observed at 0% RH, and no apparent feature forms under UHV (Figure 3A−C). These experiments suggest that unless one moves to rigorous UHV conditions, water collects at the point-of-contact regardless of the relative humidity of the chamber used to confine the experimental apparatus. Although the experiments described previously are compelling, they are not completely unambiguous because they are an indirect indication of meniscus formation and do not take into account potential mechanical damage induced by the tip.

Adhesion Forces as a Function of Humidity using a Hydrophilic Tip. To attempt to differentiate the effects of mechanical deformation of the surface from meniscus formation and dissolution of the NaCl, we performed a series of experiments under UHV conditions aimed at measuring force distance curves as a function of water partial pressure in the UHV chamber (Figure 4). This set of experiments also allows us to look at the difference between UHV and the 0% relative humidity conditions. In a typical experiment, the tip is brought into contact with the substrate, and a force−distance curve is measured as a function of chamber water content. The magnitude of the pull-off point (the most negative value) is a measure of the attractive interaction between the tip and the surface combined with the capillary effect.[29] As the capillary effect is reduced, the magnitude of the absolute value of the pull-off point decreases. This is exactly what is observed in our experiments on NaCl. Significantly, the absolute value of pull-off point decreases as water content is decreased (Table 1). Note that the pull-off peak at 2.1×10^{-9} Torr is approximately one-half that at 0% RH. Versions of these experiments also have been carried out on the conventional DPN platform with a similar trend observed (Figure 5A). The attractive and adhesive forces were measured in the range between 0 and 60% relative humidity, and a decrease in the pull-off peak as a function of decreasing atmospheric water content was observed (Figure 5A,B).

TABLE 1

water partial pressure	absolute value of pull-off point (nN)
2.1×10^{-9} Torr	1.85
4.7×10^{-7} Torr	2.80
RH = 0%	3.40
3.4×10^{-5} Torr	3.70
RH = 22%	8.20

Effect of Tip Hydrophobicity on Meniscus Formation. All of the experiments described previously involved a hydrophilic tip. A key question involves what happens to the meniscus when a hydrophobic tip is used. This has been explored in the context of DPN and normal AFM where our group has noted that image resolution is often enhanced when a hydrophobic ink or a hydrophobic coating made of dodecylamine is used during imaging.[9] The reason for this enhancement was explained based upon a reduction in the capillary force when compared with a bare tip. Herein, we use the NaCl dissolution experiment to probe meniscus formation (Figure 6). These experiments are more difficult to analyze than the ones described previously because they have the added complexity of a tip surface coating, dodecylamine. Dodecylamine was chosen because it is hydrophobic and is resistant to transport.[9] At 20% RH, after a dodecylamine-coated tip is brought in contact with the NaCl substrate for 1 min and then removed, imaging shows that deep pit formation occurs (Figure 6A,B). This is reminiscent of what happens with the bare hydrophilic tip but to a lesser degree (Figure 6C,D). Oftentimes, unusual shapes such as rings rather than uniform holes result from the dodecylamine-coated tip. This could be due to the shape of the meniscus or the residual dodecylamine protecting the point of contact from dissolution.

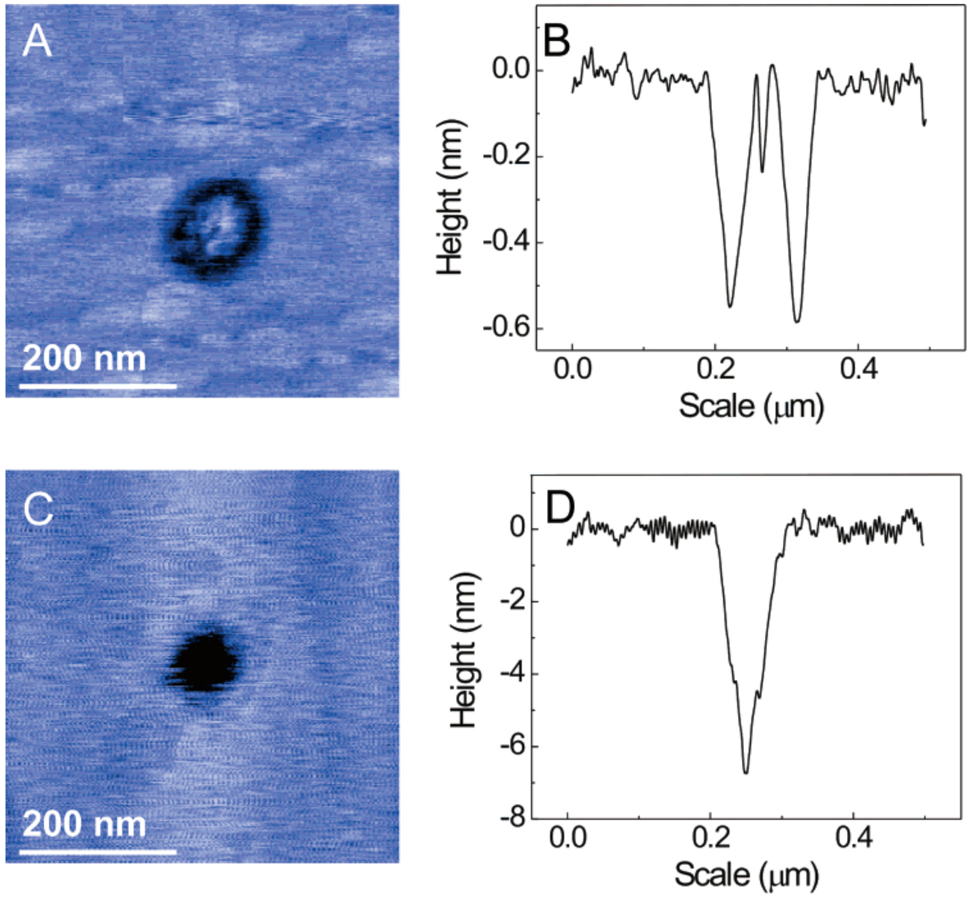


Figure 6. AFM images and topography profiles of the pits formed by (A and B) a tip coated with dodecylamine and (C and D) a bare tip. The contact force was 1 nN, and the relative humidity was 20%.

Regardless, the experiment clearly shows that even with a hydrophobic tip, water will move near the point of contact between tip and surface and form a meniscus (Scheme 1B). Finally, the pull-off point measurements as a function of humidity in the case of dodecylamine-coated tips do not prove to be an effective means of measuring the water near the point-of-contact (Figure 5C,D). Apparently, the attractive forces between hydrophobic tip and water in the meniscus are weak enough to not significantly contribute to the absolute value of the pull-off point.

Conclusion

Two types of experiments were used to study meniscus formation at the point-of-contact between AFM tip and sample. The first involved the use of a NaCl crystal and looked at the dissolution of the NaCl at the point-of-contact as a function of relative humidity. Water moved to the point-of-contact under all conditions studied, except UHV. Similarly, force–distance measurements were used to determine when water was at the point of contact. Significantly, the absolute value of the pull-off points decreased as a function of decreasing system water content, and the absolute value of the pull-off point under UHV conditions was significantly smaller than at 0% relative humidity conditions, demonstrating that even under dry conditions, water will be at the point-of-contact, and therefore, influence imaging as well as ink transport in a DPN experiment. Meniscus formation occurs even when tips are coated with a hydrophobic layer like dodecylamine, albeit the magnitude of the effect is significantly reduced. Finally, these experiments show that unless one goes to great lengths (a baked-out UHV chamber) to eliminate water from a DPN apparatus, water will always be between the tip and the surface and will influence AFM measurements as well as ink transport. In many cases, the water will aid in transport, but in some, as in the case of ODT, it can have a mild inhibiting effect.[17,19]

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