In Situ Imaging of a Detergent Monolayer Using Scanning Tunneling Microscopy

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Scanning tunneling microscopy (STM) is a technique capable of providing atomic resolution images of surfaces in vacuum, air, and liquids. By use of STM a biological membrane model system consisting of a detergent monolayer adsorbed onto the surface of graphite has been imaged with high resolution in aqueous solution. The imaging results demonstrate that it is possible for tunneling to be efficient in biological systems despite their low bulk conductivities.

Introduction

Scanning tunneling microscopy (STM) is a new technique that can provide atomic-resolution three-dimensional images of surfaces.[1] The underlying basis for this important technique is electron tunneling between a sample surface and a metal tip. Tunneling can occur when the wave functions on the surface and the tip overlap. The tunneling current (I_t) that flows when a voltage is applied between the sample and the tip is highly dependent on this orbital overlap, and thus the tunneling current can be used as a sensitive probe of the structural and the electronic properties of interfacial systems. Although much of the work in this field has focused on the investigation of metal and semiconductor interfaces in vacuum,[1,2] recent studies have demonstrated that surface images can also be obtained in air[3] and liquids.[4] Hence STM should be able to provide heretofore unavailable high-resolution data applicable to many problems in chemistry and biology.

One such area involves using the STM to image biological molecules under conditions close to which they function. However, biological materials typically have low conductivities, and thus the tunneling experiment is more difficult to carry out than with metallic and semiconducting materials. To avoid such difficulties several researchers have used STM to image conducting replicas of membranes[5] and DNA[6] prepared by evaporating metal and/or carbon onto the surfaces of the biological samples. STM images also have been obtained for uncoated air-dried samples of DNA,[6b,7] a bacteriophage,[8] and a phosopholipid membrane,[9] but with limited resolution. The low resolution of these experiments was attributed to the poor conductivity of the samples.[5] On the other hand atomic resolution images have been obtained for bilayers prepared by the Langmuir–Blodgett technique.[10,11] These results are particularly intriguing because the reported high conductivities suggest that tunneling can occur efficiently over distances as large as 50 Å.

In this Letter we report new imaging results of a model-membrane system that consists of a monolayer of the detergent 3-[(3-cholamidopropyl)dimethylammonio]-1-propanesulfonate (CHAPS, Figure 1)[12,13] adsorbed on the surface of highly oriented pyrolytic graphite (HOG) in aqueous solution.

Experimental Section

All STM images were acquired with a modified[14] commercial instrument (Nanoscope I, Digital Instruments, Santa Barbara, CA) that was operated in the constant-current mode.[1] Images were recorded in real time (typically 5–10 s/image) by using an analog storage oscilloscope. The oscilloscope traces were then photographed for display. Lighter areas in these images correspond to increased to tip–sample separation; increases/decreases in separation, necessary to maintain a constant tunneling current, are due to electronic and structural variations at the interface. Platinum–iridium wire (90:10) was used for the tunneling tips; tips capable of atomic resolution were prepared mechanically or by electrochemical etching.[4c]

Oriented graphite crystals (Union Carbide Corp., Parma, OH) were used for the conducting substrate in our studies because they can be cleaved to give atomically flat hydrophobic surfaces that readily adsorb the hydrophobic tails of detergents. Aqueous solutions of CHAPS (Calbiochem, La Jolla, CA) were prepared by using deionized water (17 Mohm) to reduce ionic currents that can often exceed the tunneling current.[4] Because CHAPS is a zwitterionic detergent it does not contribute to these ionic currents.[12] Monolayers of CHAPS were prepared in situ by placing several drops of ca. 5 mM solution on the surface of a freshly cleaved sample of HOG. The surface was then imaged through unevaporated solution.

Results and Discussion

A 20 × 20 Å image of a monolayer of CHAPS on the graphite substrate obtained in situ is shown in Figure 2a. The periodic array of white spots have an average separation of 4.4–4.6 Å in the horizontal direction and 3.5–3.6 Å in the vertical direction. For comparison an image of the graphite surface recorded at the same magnification but at a higher tunneling current is shown in Figure 2b; the regular hexagonal pattern, 2.4–2.5 Å peak spacing, is typical for images of this material.[1,3] The asymmetry observed in the CHAPS monolayer image may be due to the nature of the molecular packing,[12] the unequal x and y scan frequencies, and/or mechanical interactions with the tip.[11] The latter two possibilities are unlikely because variations in the x and y scan frequencies from 15 to 25 and 0.1 to 0.2 Hz, respectively, produced little change in the observed images. We find that images such as Figure 2a can be obtained when the concentration

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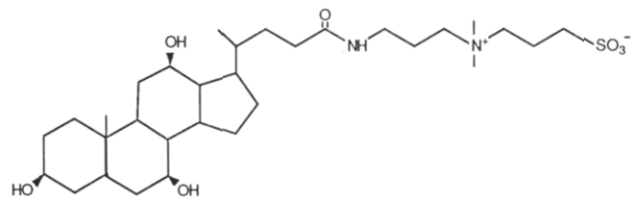

Figure 1. A view of the carbon skeleton of a CHAPS detergent molecule. Hydrogen bonding between the hydroxy groups on adjacent molecules can stabilize the monolayer.[12]

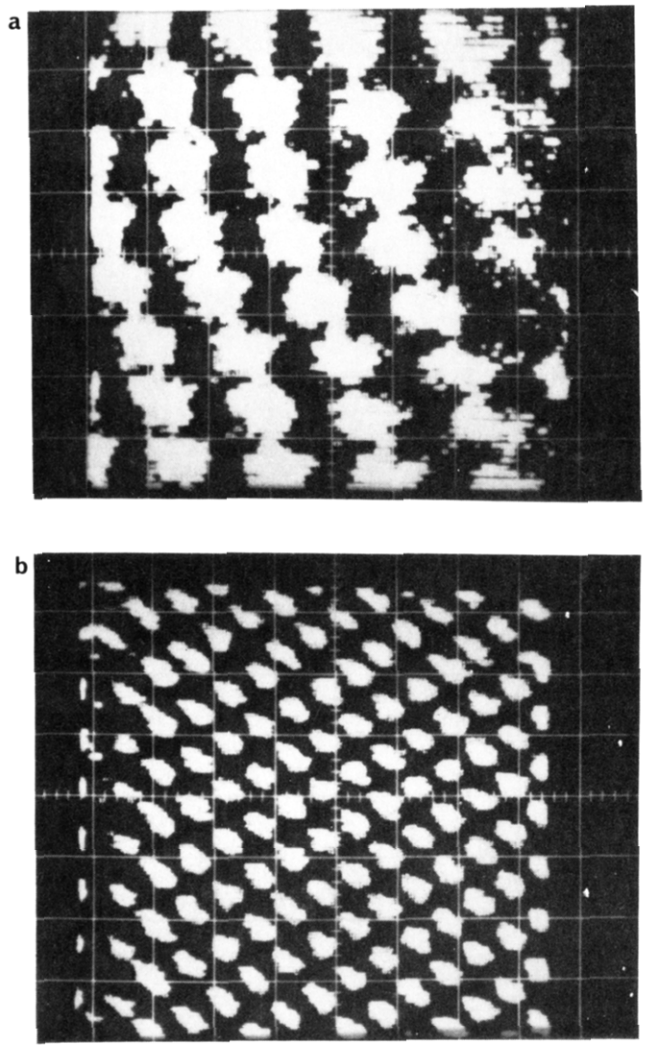

Figure 2. (a) A 20 × 20 Å top-view image of the monolayer recorded while tunneling through a 5 mM aqueous solution of CHAPS with the following STM parameters: (i) I_t = 0.75 nA, (ii) the sample biased at −0.1 V relative to the tip, and (iii) the horizontal and vertical scan frequencies at 18 and 0.15 Hz, respectively. (b) The 20 × 20 Å top-view image recorded for the same sample by using identical STM parameters except that the tunneling current was increased from 0.75 to 2.0 nA.

of CHAPS in solution is near the critical micelle concentration (7–10 mM).[13] The ordered monolayer tunneling pattern (Figure 2a) was also observed over areas as large as 100 × 100 Å, but the tunneling current peaks are less well resolved than when the images are of smaller areas. If the solution of CHAPS on HOG was allowed to evaporate, similar images could be obtained, although with greater difficulty. In addition, these images were more stable to changes in the tunneling current, vide infra.

We believe that the observed STM images of CHAPS were recorded while scanning the tip above the surface of the monolayer and hence tunneling through CHAPS. In support of this conclusion we find that the magnitude of the tunneling current set-point is critical to successful in situ imaging of the CHAPS monolayer.[15] Notably, when I_t was increased above 1.5–2 nA the monolayer image abruptly disappeared and was replaced by an image of the graphite surface. In addition, there is an increase in the z-piezo voltage of about 1.1–1.3 V at this point which corresponds to a 22–26-Å movement (the estimated thickness of a CHAPS monolayer) of the tip toward the graphite surface. Parts a and b of Figure 1a were recorded sequentially in this manner. For several samples, when I_t was again reduced below 1–1.5 nA, the CHAPS monolayer image reappeared. This behavior suggests that the CHAPS molecules in the monolayer cannot support tunneling currents greater than 1.5–2 nA; when this value is exceeded the feedback loop moves the tip toward the graphite and mechanically disrupts the ordered structure of CHAPS on the surface. For samples in which the solution has evaporated there is no abrupt change in the image as the current is increased. However, at sufficiently high currents (5–8 nA) the graphite surface is observed, in agreement with previously reported results.[11]

Observation of a maximum current for which the STM images of CHAPS could be recorded has important implications for understanding the mechanism of electron tunneing in these systems. If tunneling between the sample surface and tip is described by a standard one-dimensional model, the decay of I_t with distance, which reflects the decrease in tip–sample wave function overlap, should depend only on the barrier height.[16] Within the context of this model our observed results suggest that the barrier height must be about a factor of 20 lower when the monolayer is between the sample and tip. Low barrier heights have been reported for STM experiments in air and liquids.[7,17] They are believed to result from mechanical interactions between the tip and a surface adsorbate and hence could explain our observed results. An alternative mechanism that can explain the efficient tunneling observed in these systems involves direct orbital interactions between the graphite surface, CHAPS molecules, and tip. This suggestion is based on the close similarity between the STM experiment and long-range electron-transfer (ET) reactions. In fact, the CHAPS molecule is very similar to several ET systems for which direct orbital interactions between the ET centers and spacer ("through-bond" mechanism) have been invoked to explain the electronic coupling.[18] Notably, the one-dimensional tunneling model cannot adequately explain the distance dependence of ET in these systems.

In conclusion, we have used STM to obtain the first atomic resolution images of an ordered detergent monolayer in aqueous solution. The efficient tunneling observed in these systems may be due to very low barrier heights or to direct electronic (or orbital) interactions with the CHAPS molecules in the monolayer. Investigations of tunneling through monolayers of different chemical composition (i.e., with unsaturated sites) and different lengths are in progress and should help to clarify the mechanism of tunneling in these systems. These and other results will be useful for obtaining a better understanding of electron tunneling over long distances and for developing STM as a tool for imaging biological molecules.

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(15) Although the magnitude of the tunneling current is critical for successful in situ imaging, both positive and negative bias voltages, |0.05–0.12 V|, have been used to obtain images of the monolayers.

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