STM in a Gel Environment

J.W. Gerritsen, J.A.A.W. Elemans , B. Hulsken, A.M. Travaille, H. van Kempen, Th. Rasing, S. Speller.

NSRIM Institute , University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands
Email address corresponding author: sspeller@sci.kun.nl

Abstract. A gel can be used as an environment for STM measurements with excellent stability. Our gelator molecule is stearic acid and the confined solvent can be one of the solvents that are commonly used in STM imaging at liquid-solid interfaces. In addition to the gelator molecules themselves, also other molecules included in the gel can self-assemble at the gel-solid interface. In this case there is a competition between the gelator molecules and the additive for a position at the interface.

INTRODUCTION

STM is a powerful tool to study the organization of molecules in self-assembled layers on a variety of substrates. Formation of these monolayers is often carried out in a drop of almost saturated solutions of molecules which is placed on the surface, after which images of the molecules at the liquid solid interface can be obtained[1]. In general, liquids with a high boiling point and a low vapor pressure are used, such as phenyloctane, tetradecane, 1,2,4-trichlorobenzene, etc. Recently it has been demonstrated that for certain combinations of molecules and solvents the formation of a gel occurred, and the rigidity of the STM tip allows scanning and imaging in this environment[2]. The slow evaporation of the solvent that is captured within the gel is the reason that this environment is very stable for several days.

We have prepared a simple gel using cheap components: stearic acid as the gelator with e.g. phenyloctane or tetradecane as solvent. A gel constructed in this way shows a reliable formation of a monolayer of the stearic acid gelator molecules when applied on a freshly cleaved HOPG substrate. More importantly, it allows routine imaging of the molecules at the gel-HOPG interface for more than 5 days. AFM experiments showed the network of molecules in the gel, but it was also demonstrated how easily this network is damaged by scanning in tapping mode.

Many other molecules are known to self-assemble on a surface and we tried to utilize the gel medium as a carrier/matrix for alkane-substituted porphyrin molecules, which compete with the stearic acid molecules for a position at the gel-solid interface. After some time, the porphyrin molecules displace the stearic acid and show up at the gel-HOPG interface.

CP696, *Scanning Tunneling Microscopy/Spectroscopy and Related Techniques: 12th International Conf.,*
edited by P. M. Koenraad and M. Kemerink

RESULTS AND DISCUSSION

The gel was prepared by heating a small amount of stearic acid in phenyloctane (or e.g. tetradecane) slightly above the melting temperature of the gelator (70 ^{o}C). Upon cooling down the mixture, a stable and transparent gel was formed.
A thin layer of the gel was prepared by gently blowing away, with a nitrogen gas flow, a thick drop of the gel which was deposited onto a freshly cleaved mica substrate. It was then studied by tapping mode AFM. Scanning revealed network-like structures, which were damaged when subsequent scans were carried out in the same region. Figure 1 shows a region of which the structures in the center were damaged during earlier scans of a smaller frame. In the center, an area is observed which is 'cleaned'. In addition, some fibers, networks of fibers, and around the damaged part islands where the solvent is still present can be observed.

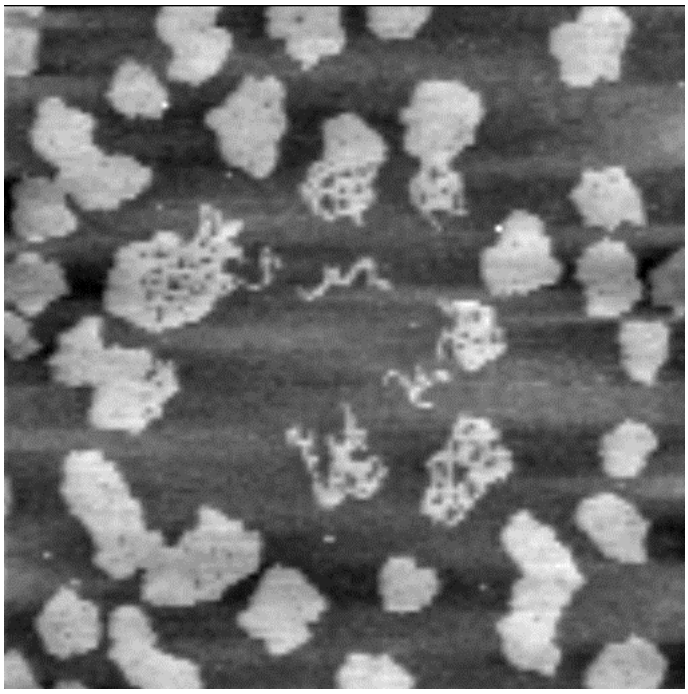

FIGURE 1. Tapping mode AFM image of a very thin layer of the gel after several scans in the center of the image. Fibers can be clearly distinguished, and in addition networks and the islands of the gel substance. The height difference is 1 nm, the x and y scan size is 5 * 5 μm.

Figure 2 shows that in the STM setup the tip and sample are completely covered with the gel, which is ready for imaging. The STM we have used is a home-built system [3] which is optimized for scanning with tunneling currents down to 1 pA. under ambient or liquid conditions. Upon scanning the gel, large domains of the stearic acid gelator molecules, self-assembled at the gel-HOPG interface, can be imaged with submolecular resolution (Figure 3). Stable scanning and imaging is possible even after several days. The main driving forces for the self-assembly of the molecules are the formation of dimers by double hydrogen bonding between the

carboxylic acid groups, and the presence of the long alkyl tails that are known to deposit favorably onto a HOPG lattice.[4]

FIGURE 2. The tip and sample of our home-built STM immersed in a gel which allows scanning for several days at the gel-HOPG interface. In the center of the image we see the tip and the gel-covered HOPG.

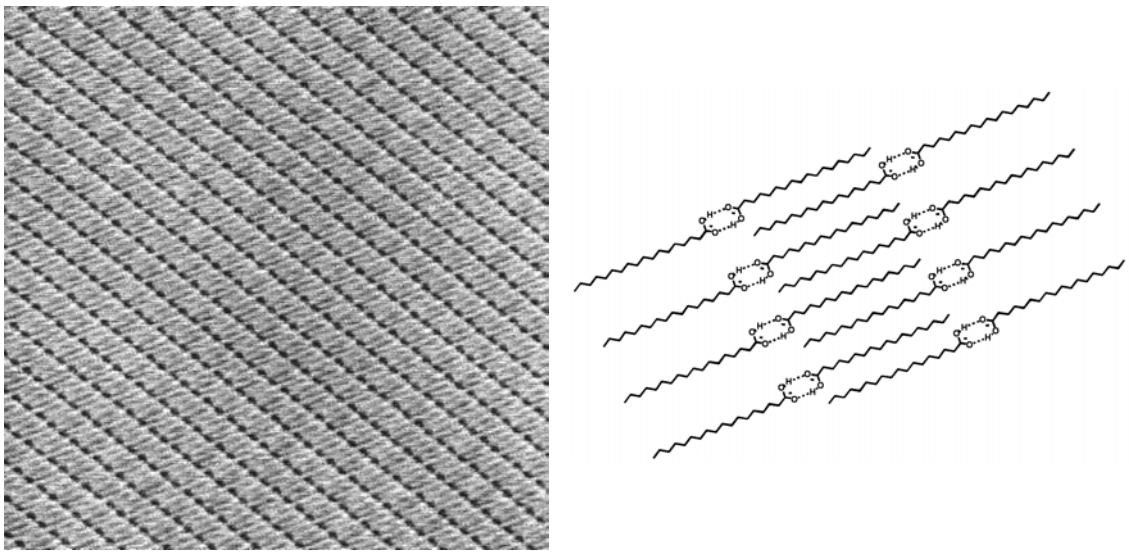

FIGURE 3. Stearic acid molecules self-assembled from the gel at the gel-HOPG interface. Scan size 50 * 50 nm. V_{sample} = -730 mV, i_{bias} = 6 pA. height difference 0.06 nm.

An even more interesting result is achieved if we also add porphyrin molecules, functionalized with four C11 alkyl tails, to the gel. These molecules, which are known to form stable self-assembled monolayers at the HOPG-phenyloctane interface, have to compete with the large amount of stearic acid molecules present in the gel for a position at the gel-HOPG interface. After some time, we could however image the porphyrin molecules at the interface instead of the stearic acid molecules, which apparently have been displaced.

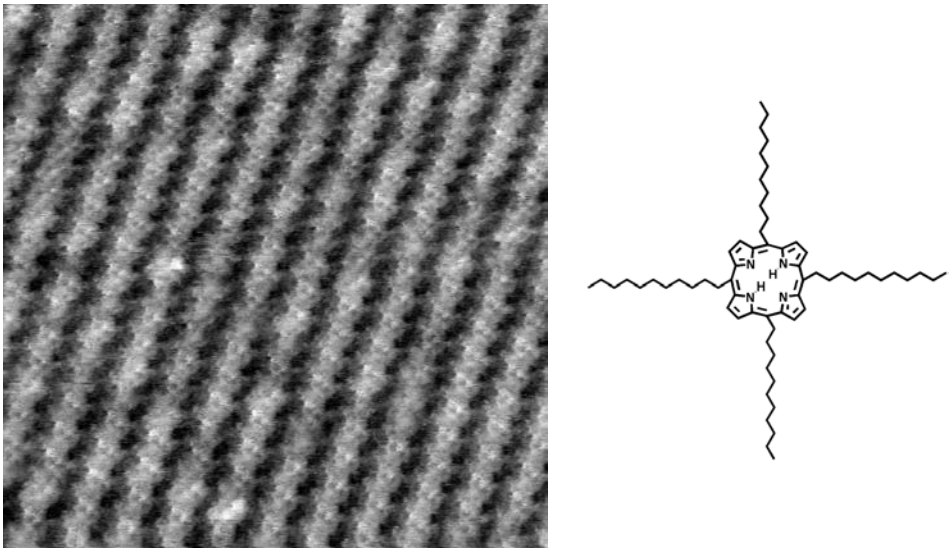

FIGURE 4. Porphyrin visualized at the stearic acid gel-HOPG interface. Scan size 30 * 30 nm. V_{sample} = -0.82 V, i_{bias} = 8 pA. Height difference 0.2 nm.

CONCLUSION

It has been demonstrated that in a gel of stearic acid and phenyloctane (or tetradecane) a monolayer of the stearic acid molecules is organized at the gel-HOPG interface. In this gel it is also possible to assemble and visualize other molecules (in our case porphyrins) at the gel-substrate interface.
Our current research is aimed at the application of this gel to substrates where regular patterns of the stearic acid molecules are not observed, such as gold or silver surfaces. Our aim is to add molecules to the gel that usually do self-assemble at these surfaces to increase the lifetime of the self-assembled layers.

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