Special features in self-assembled monolayer revealed by functionalised STM tips

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Abstract. Some functional groups in self-assembled monolayers have recently been identified in STM images, due to the chemical modification of gold tips [1]. In those studies, different molecules presenting different functional groups were investigated, resolving several molecular organizations [1-2, 4]. In this paper, we aimed at demonstrating that such chemically modified STM tips can be used to investigate phenomenon routinely observed with standard Pt/Ir tips, such as domain boundary dynamics in hexadecanol SAMs. It also allows transitory features to be identified. Moreover, rarely observed phenomena are also presented below, i.e. bilayers composed of wax esters molecules physisorbed at the phenyloctane/graphite interface.

1. Introduction
Previous research results pointed out all the advantages using chemically modified scanning tunneling microscopy (STM) tips in self-assembled monolayers (SAMs) imaging [1-2]. The most important one is certainly the ability of highlighting functional groups which are usually not identified in STM images. This phenomenon was explained as a consequence of the formation of hydrogen bonds between the functional groups on tip and sample, making easier electron tunneling. In this case, the tip chemical modifications are performed by binding molecules at gold tip apex. The bound molecules are mercaptobenzoic acid (MBA) and mercaptotoluen (MT) molecules.

For example, this technique was applied to the identification of fatty acid and ester’s molecular organization at the liquid/solid interface. It allowed the first STM imaging of wax ester molecules and the ester group’s position and orientation inside the molecular assembly [1]. It also unambiguously confirms the adsorption model of fatty acids molecules elaborated by Hibino and coworkers [2-3]. Moreover, it discriminates zinc and metal-free porphyrin centers [4].

In this paper, we aimed at demonstrating that can be observed with functionalized tips special features commonly and/or rarely observed on SAMs with standard STM tips. Particularly, dynamical processes were first observed in alcohol SAMs. This allowed the identification of transitory organizations at surface. Bilayers structures of wax esters layers were then exposed.

2. Experimental
Experiments are performed with a commercial STM (Nanoscope IIIa, Digital Instruments) under ambient conditions. Highly oriented pyrolic graphite (Advanced Ceramics, ZYH grade) is used as substrate. Alcohols (hexadecanol, HD) and wax esters (Palmitoyl palmitate, PP) molecules are
purchased from Aldrich and used without further treatment. They are dissolved near saturation in phenyloctane (Aldrich).

During a scan, the tip is immersed in several drops of the solution, deposited on the freshly cleaved graphite substrate. The liquid/solid interface is then imaged with the STM operating in the constant current mode with functionalized STM tips. A zero-order flattening procedure is used to normalize the vertical offset produced.

STM tips are prepared from gold wire (0.20 mm diameter, Goodfellow, England; 99.99 %) by mechanical cutting. Before cutting, tips are washed by sonication in ethanol and further dipping in piranha solution (7:3 concentrated H₂SO₄/H₂O₂. Caution: piranha solution reacts violently with organic compounds and should not be stored in closed containers). Tips are finally washed again in ethanol. The functionalization is realized through the binding of molecules on the STM tip. We therefore immerse them for 12 hours in a saturated 4-mercaptobenzoic acid (MBA; Aldrich, 97%) or 4-mecaptotoluen (MT; Aldrich) solution in ethanol. They are then rinsed with ethanol and dried in a stream of nitrogen.

3. Results

Chemically MBA- and MT-modified gold tips are used for the STM imaging of special features on self-assembled monolayers. The carboxyl and methyl terminal groups of those tip functionalizing molecules are assumed to interact with functional groups in the SAM. This interaction lead to the enhancement (or not) of the contrast observed in the STM image [1].

As an example, let’s have a look at Figure 1. It presents the structure of a hexadecanol self-assembled monolayer at the phenyloctane/graphite interface, imaged with MBA- and MT-modified STM tips in Figs 1A and 1B, respectively.

![Figure 1: STM image of hexadecanol self-assembled monolayer imaged with (A) MBA- and (B) MT-modified STM gold tips (30 nm x 30 nm). (C) Schematic model structure of the hexadecanol molecular organization at the phenyloctane/graphite interface. Arrows indicate the position of the hydroxyl groups.](image-url)
with the model structure presented in Fig. 1C, as determined by several research groups [5-6], where hydroxyl groups (black circles) are facing each other in order to favor hydrogen bond formation.

Moreover, MT-modified gold tips allow us to also observe evolution of domain boundaries in those SAMs, as shown in Figure 2. The images presented therein are obtained under identical conditions and results from successive data. As revealed in Fig. 1B, hydroxyl groups are appearing as bright lines. This is also the case for images of Fig. 2. Therein, several domains are observable and oriented in different or identical directions (as highlighted by the bright lines). For example, in Fig. 2A domains I and II, III and IV, V and VI are oriented by pairs in the same direction.

Thereafter, as highlighted by white lines, domains limits are rapidly modifying. These are clear illustrations of dynamical processes occurring at domain boundaries. Indeed, the alkanol overlayers is in equilibrium with the supernatant solution. The molecular movements in the SAM therefore reflect a balance between molecule-molecule and molecule-substrate interaction. Moreover, Figs 2A to 2J highlight the disappearing of small domains while larger domains grow at their expense. Indeed, six domains are observed in Fig. 2A, against only three in Fig. 2J. Such processes can be related to Oswald ripening and have been intensively studied in previous work with standard tips [7-8].

**Figure 2:** Evolution of domain boundaries in hexadecanol SAMs at the phenylcane/graphite interface. Images (A) to (J) were obtained under identical conditions and results from successive data. Domain boundaries are highlighted by white lines. (K) Schematic model structure of the hexadecanol organization, as indicated by arrows in image (C).

Another important observation can be revealed in the early stages of this dynamical sequence. At different regions, we can see strange things, i.e. the bright lines (corresponding to the alignment of
hydroxyl groups) are not equally distributed, as indicated by white arrows in Fig. 2C. Those bright lines are separated by about 2.5 nm and 4.6 nm, which respectively correspond to about one and two molecules’ length. This therefore seems to denote different molecular organization at the liquid-solid interface. Based on the model presented in Figure 1C, the structure proposed is quite simple, as can be seen in Figure 2K. There, some bilamellar structures (due to hydrogen bonding between facing hydroxyl groups) are separated by a single lamellae (not bound by hydrogen interactions). This model agrees well with the measured lamellae width of about two and one molecule length. Such single lamellae structures are present in Fig. 2A to 2H. However, they progressively disappear, as they are not visible in Fig 2I and 2J anymore. This seems relatively evident as the single lamellar structures are more mobile than the bilayer ones, which are stabilized by hydrogen bonding between molecules.

We also observed peculiarities on other self-assembled monolayers. Particularly, we could observe bilayer structure in wax ester SAMs with MBA-modified gold tips, as presented in Fig. 3A (in the white rectangle). The structural description of wax esters monolayers has been largely described elsewhere. To resume, the SAM structures in lamellae, separated by troughs and composed of lying molecules with their molecular axes oriented at about 60° related to troughs directions. The ester groups are pointing out of the substrate surface [1]. In the bilayer imaged, the uplayer seems to be composed of parallel sticks, oriented in the same direction as the underlying layer. There is no observable rotation of molecular lattices on one layer relative to the other. From Fig. 3B, we can observe the obvious height difference between the two layers of molecules. According to this cross sectional profile, the upper layer is measured to be about 1Å higher than the lower one. This seems relatively low. However, it must be taken into account that this measured height is due to electron tunneling through two poorly-conductive molecular layers (plus one molecule on the tip).

Notice that, as suggested by the dark trough (highlighted by a white arrow in the lower part of the image) and confirmed by subsequent images on the same area, the upperlayer is sliding on the grain boundary, probably pushed by the STM tip.

Further, it can be observed that the upperlayer is located at a grain boundary of the lower layer, as the left and right underlying SAM are shifted vertically (as highlighted by the blue line in Fig. 3A). It can therefore be assumed that defect sites as grain boundaries, promotes the formation of bilayer structures.

4. Conclusion
Hydroxyl groups in hexadecanol self-assembled monolayers have been identified in STM images, due to the chemical modification of gold tips. In those SAMs, we demonstrated that such chemically modified STM tips could be used to investigate phenomenon routinely observed with standard Pt/Ir tips, such as domain boundary dynamics. Transitory phenomena (i.e. monolamellar structures) have
been identified. Moreover, rarely observed are bilayers structures in wax esters SAMs physisorbed at the phenyloctane/graphite interface.

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6. References
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