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STM tip functionalisation:

A route to chemical contrast imaging

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Abstract

The influence of the modification of a STM tip on the image contrast is investigated. This revolutionary technique is applied to the identification of the molecular organisation inside self-assembled monolayers (SAMs) of wax esters. Moreover, the contrast difference observed, while imaging with two different tip modifications, highlights the ester group position and orientation. The application of this process to the study of fatty acids overlayers demonstrates its transposability to other compounds.

Introduction

Atomic resolution imaging is possible since the invention of the scanning tunnelling microscope (STM) by *Binnig* and *Röhrer* 25 years ago [Binnig1981]. Actually, it would be more appropriate to talk about “nanoscopy”, because it makes feasible the observation of individual atoms and molecules. At that time, surface organisation and reconstructions were the aims of important studies. This microscopy opened new perspectives concerning surface analysis, particularly in the domain of nanotechnology.

Since many years, STM users were dreaming of identifying the chemical composition of the imaged structures. Indeed, the knowledge of the structure and composition at the atomic scale would be of considerable interest in the elaboration of new nanotechnological applications. Considering the STM configuration, the overlap of the electronic wave functions of sample and tip is responsible for tunnelling. It can therefore reasonably be assumed that a tip modification involves a change in the tip electronic configuration and hence modifies the contrast of the imaged structures. Binding molecules to the tip, as already demonstrated, can easily induce such changes. For example, it was reported that CO molecules on a STM tip achieved chemical contrast, allowing distinction of CO molecules and oxygen atoms adsorbed on Cu(111) [Bartels1997]. Unfortunately, most of those experiments are performed under ultra-high vacuum, making it difficult to use under ambient conditions for rapid and precise analysis of adhesion or lubrification phenomena, for example.

We therefore tried to transpose to ambient conditions such tip modification, allowing chemical contrast imaging. In this context, we used gold tips, which were chemically modified by 4-mercaptobenzoic acid (4MBA, Fig. 1) and 4-mercaptotoluen (4MT). The chemical contrast induced is checked on self-assembled monolayers containing esters and carboxylic groups, which are not identified in the usual STM images. Particularly, we report on a STM study of wax ester (palmitoyl palmitate) and fatty acid (lauric acid) layers at the phenyloctane/graphite interface.

Materials and methods

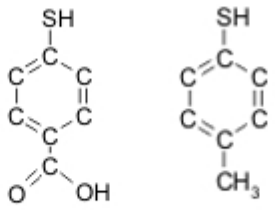

Figure 1. Chemical structure of molecules functionalising the tips. (Left) 4-mercaptobenzoic acid (4MBA). (Right) 4-mercaptotoluene (4MT).

Experiments are performed with a commercial STM (Nanoscope IIIa, Digital Instruments) under ambient conditions. Highly oriented pyrolitic graphite (HOPG) is used as substrate (*Advanced Ceramics*, ZYH grade). Palmitoyl Palmitate (PP) [CH_3-$(CH_2)_{14}$-CO-O-$(CH_2)_{15}$-CH_3] and lauric acid [CH_3-$(CH_2)_{10}$-COOH] are purchased from *Aldrich* and used without further treatment. They are dissolved near saturation in phenyloctane. During a scan, the tip is immersed in several drops of the solution. The liquid/graphite interface is then imaged with the STM operating in the constant current mode. A zero-order flattening procedure is used to normalize the vertical offset. Experimental results are reproducible, but not predictable. Typically, many trials are required before ordered layers are observed. We found that ordered layers are easily visible during the experiments performed with modified tips when the solution's layer is very thin.

STM tips are prepared from gold wire (*Goodfellow*; 99,99 %) by mechanical cutting. Before cutting, the wire is rinsed by sonication in ethanol and further dipping in piranha solution (7:3 concentrated H_2SO_4/H_2O_2. *Caution: piranha solution reacts violently with organic compounds and should not be stored in closed containers*). Tips are finally rinsed again in ethanol. For the formation of self-assembled monolayers on tips, we immerse them for 12 hours in a saturated 4-mercaptobenzoic acid (4MBA; *Aldrich*) or 4-mecaptotoluen (4MT; *Aldrich*) solution in ethanol. The tips are then rinsed with ethanol and dried in a stream of nitrogen.

Results and discussion

Previous studies pointed to the difficulties of obtaining reproducible and interpretable results on wax esters SAMs with standard Pt-Ir tips [Istasse1999]. The resolution at the scale of molecular organization is not achieved despite a considerable number of trials. Moreover the position of the functional groups is not revealed by the STM data, as also observed with bare gold tips.

Structural imaging

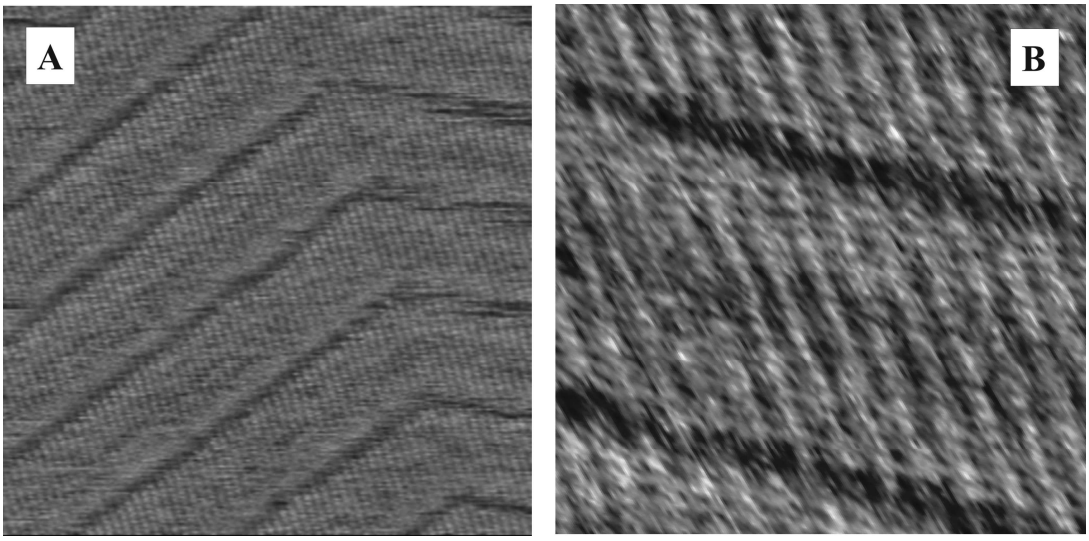

Figure 2. (A) STM image representing part of a domain boundary in PP SAMs, obtained with a 4MBA gold tip (25nm x 25nm, 740pA, -485mV) (B) High-resolution STM image of PP lamella obtained with a 4MBA modified gold tip (6nm x 6nm, 740pA, -485mV).

Figure 2A highlights lamellae of PP SAMs, separated by troughs (less than 2Å deep) repeating every 5nm. They also seem to be formed by an arrangement of parallel sticks, oriented at about 60 degrees with respect to the troughs. Figure 2B is a high-resolution image of one ester lamella. There, individual sticks can be distinguished. They are approximately 3.9 nm long, which is about one molecule length. The number of bright spots forming the sticks is evaluated around sixteen. This structure can be interpreted as a two-dimensional array of ester's molecules at the liquid/graphite interface. Molecules are lying on the surface with their axis parallel to the surface. The

length of the sticks, forming the lamellae, is in good agreement with the length of ester's molecules measured from XRD experiments [Istasse1999]. Moreover, the number of spots forming sticks indicates that the molecules are lying on the substrate with the plane formed by their carbon chain perpendicular to the substrate. We can therefore confirm that, with functionalised STM tips, we can observe what is routinely observed with standard tips. Moreover, those former results reveal better contrast and image quality.

Chemical contrast imaging

The comparison between images obtained with 4MBA and 4MT modified gold tips reveals the ester group position within the molecule. Such tips enhance the contrast between ester and methylene groups inside the molecule. Indeed, recent studies put in evidence that they can be applied for the identification of several functional groups, hardly visible otherwise [Ito1998, Volcke2005a, Volcke2005b].

Figures 3A and 3B present similar structural organization, i.e. adjacent lamellae composed of parallel sticks. However, as observed in the insets, a different molecule functionalising the tip (4MBA or 4MT) provides different image contrast at the centre of the trough, i.e. at the ester group position. Indeed, between each adjacent trough, small depressions with a 4MBA tip and small mounds with a 4MT tip are clearly visible.

Observations deduced from Figures 4 are quite similar. SAMs of lauric acid molecules are shown. Their molecular organization is composed of adjacent lamellae, formed by an arrangement of parallel sticks, perpendicularly oriented with respect to the troughs. The contrast observed with standard Pt-Ir tips is similar to this one obtained with 4MBA gold tips (Figure 4A). Other research groups previously observed (with standard tips) and deduced that the width of the bright bands corresponds to the length of

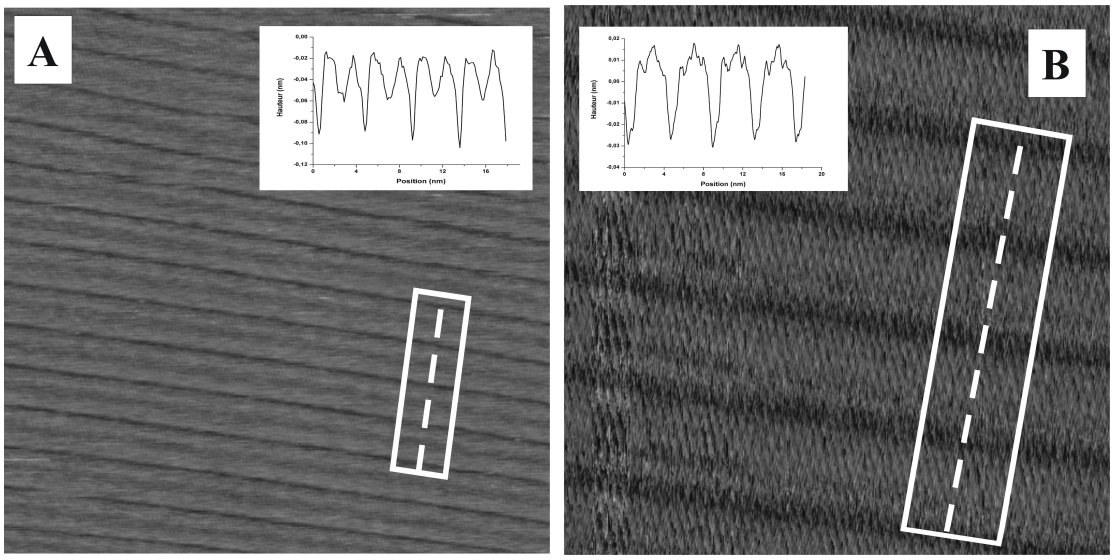

Figure 3. STM images of a PP layer at the phenyloctane/graphite interface (A) obtained with 4MBA modified gold tip (60nm x 60nm, 740pA, -485mV). Inset: line profile along the dashed line and averaged on all the line profiles laying in the white rectangle. (B) obtained with 4MT modified gold tip (23.5nm x 23.5nm, 490pA, -500mV). Inset: line profile along the dashed line and averaged on all the line profiles laying in the white rectangle [Volcke2005a].

the alkyl chain of the fatty acid. The dark regions between the bands correspond to the carboxyl groups. It was also postulated that the long axis of the molecules lies on the basal plane of HOPG [Hibino1996]. The contrast revealed by using 4MT modified gold tip is quite different. Bright spots are now visible at the troughs position (Figure 4B). So, dark spots with 4MBA gold tips and bright spots with 4MT gold tips are observed at the carboxyl group position, which is the only reactive part of the molecule.

Thus, a different chemical used to functionalise the tip (4MBA or 4MT) provides a different image contrast of the functional group (Figs 3 and 4). This phenomenon is explained as a consequence of the (un)easiness of electron tunnelling through the overlap of the electronic wave functions by the interaction between tip and sample, as described in the literature [Ito1998]. *Ito* et al. explained such contrast modification as a consequence of the hydrogen bond formation between functional groups on tip and sample, making electron tunnelling easier [Ito1998]. Insets in Figures 3A and 3B also indicate that the same functional group on sample is “seen” differently when imaged with different modified tips. Following the interpretation of *Ito* et *al.*, the interactions

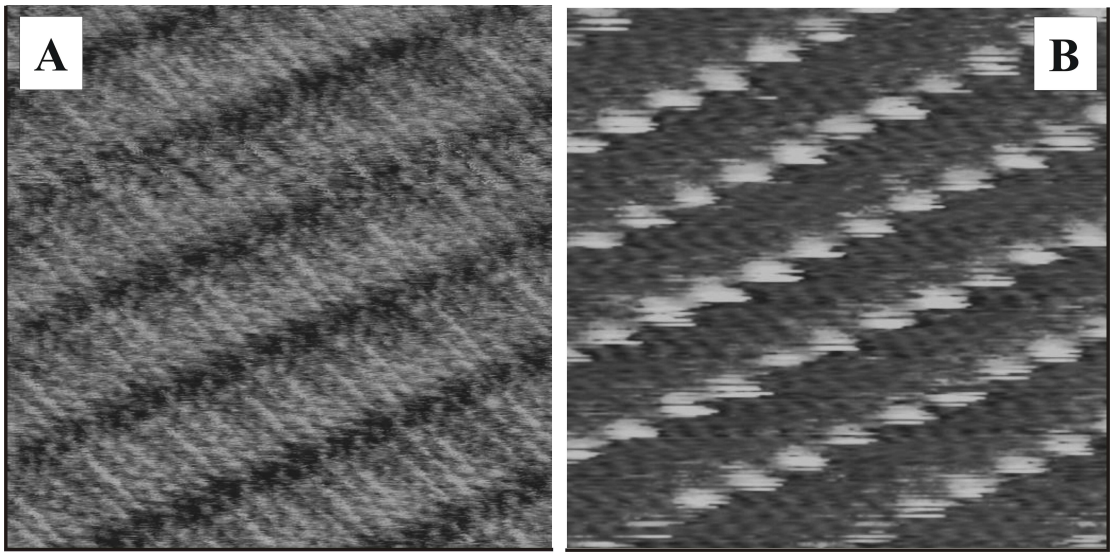

Figure 4. STM pictures of lauric acid monolayers at the phenyloctane/graphite interface (A) obtained with 4MBA gold tip (10nm x 10nm, 585pA, -520mV) (B) obtained with 4MT gold tip (10nm x 10nm, 710pA, -765mV) [Volcke2005b].

between the ester group on the sample and alkyl group “on the tip (4MT)” facilitate the electron tunnelling through the overlap of the electronic wave functions, which is not the case between the ester group on the sample and the carboxyl “on the tip (4MBA)”. These observations agree well with an ester group pointing “up” away from the graphite surface. Indeed, this organisation induces hydrogen bonding between sample and tip, leading to an overlap of the sample and tip electronic wave functions.

However, it is possible that the relaxation of atoms due to the chemical forces acting between tip and sample reduce the distance between the two electrodes and, therefore, enhance the tunneling current as a secondary effect. Resonant tunnelling between the functional group on tip and the molecular layer adsorbed on graphite may also be considered to explain the contrast variations, as developed by Tao [Tao1996].

Conclusions

In conclusion, images of two-dimensional arrays of esters are obtained at the phenyloctane/graphite interface using a scanning tunnelling microscope. Molecular organization was determined and confirmed. High-quality images

obtained with functionalised gold tips indicate that the molecules are lying on the substrate with the plane formed by their carbon chain perpendicular to the substrate. Moreover, the image contrast difference obtained with the modified tips reveals the position and orientation of the ester group, which is the only reactive part of the molecule. STM Images obtained with modified tips on fatty acids layers confirm the transposability of this technique to other systems.

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