Agilent 5600LS AFM High-resolution Imaging
Molecular-level Understanding of n-Alkanes Self-Assembly onto Graphite

Application Note

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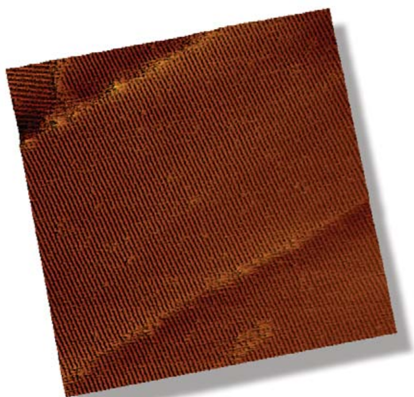

Figure 1. AFM topographic image of n-$C_{36}H_{74}$ on graphite. Scan size: 350 nm × 350 nm.

Figure 2. AFM topographic image of n-$C_{36}H_{74}$ on graphite. Scan size: 55 nm × 55 nm.

The adsorption of organic molecules from solution onto a solid surface has attracted tremendous attention as it is fundamentally associated to many phenomena of both industrial and academic relevance. Governed by an intricate balance between adsorbate-substrate and adsorbate-adsorbate interactions, spontaneous self-organization of molecules at the interface may lead to the formation of delicate ultrathin films with nanometer-scale ordered surface structures due to the molecular-level packing in a particular way. Various techniques have been reported to investigate those organic layers. For instance, differential scanning calorimetry (DSC) provides an effective means to probe the surface phase behavior. The structural information normal to the interface, to some extent, can be extracted from neutron reflectivity measurements. So far, the real time 3D structural characterization with atomic or molecular scale details of the assemblies especially the top layer comes mainly from scanning probe microscopy techniques.
In this application brief, the capability of atomic force microscopy (AFM) to directly visualize soft thin film materials with true molecular resolution is demonstrated using self-assembly of n-$C_{36}H_{74}$ molecules on graphite as an example. All the data displayed here are acquired from an Agilent 5600LS system with a 90 µm large scanner.
A typical AFM topographic image of n-$C_{36}H_{74}$ upon adsorption on HOPG is shown in Figure 1, from which rich information about this sample is revealed. First, molecules are aligned on the substrate with long-range order and exhibit a striped morphology. Second, existence of local defect areas is captured. As can be seen, the whole image is divided into four segments by two long and one short domain boundaries and a protrusion island is observed near the bottom location. Those surface features correspond to adsorbed molecules in an amorphous state. Third, two different orientations of the molecular packing are identified. The stripes in the left-upper corner are exactly 60° rotated with respect to those in the remaining three domains, reflecting the impact of underneath substrate (i.e., the 6-fold symmetry graphite) on n-$C_{36}H_{74}$ alignment on the surface. Figure 2 is another n-$C_{36}H_{74}$ / graphite topography image with a larger magnification to deliver important information at single molecular level. It shows that the stripe width is about 4.5 nm, which is matching well with the molecular length of n-$C_{36}H_{74}$ with a fully extended configuration. Furthermore, the linear backbones (i.e., hydrocarbon chains with an all-tans configuration) of individual n-$C_{36}H_{74}$ molecules are resolved at lower part of the image. These results unambiguously illustrate that n-$C_{36}H_{74}$ molecules are lying down and orderly aligned on graphite to form a lamellar packing structure.

In conclusion, AFM is a powerful surface characterization tool with an unprecedented high-resolution. Materials surface structures with sub-5 nm size in lateral dimensions can be resolved clearly, thus making it possible to achieve molecular-level understanding of the adsorption behavior of long-chain molecules at the solid-solution interface.

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