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Moiré pattern induced by the electronic coupling between 1-octanol self-assembled monolayers and graphite surface

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Abstract

Two-dimensional self-assembly of 1-octanol molecules on a graphite surface is investigated using scanning tunneling microscopy (STM) at the solid/liquid interface. STM images reveal that this molecule self-assembles into a compact hydrogen-bonded herringbone nanoarchitecture. Molecules are preferentially arranged in a head-to-head and tail-to-tail fashion. A Moiré pattern appears in the STM images when the 1-octanol layer is covering the graphite surface. The large Moiré stripes are perpendicular to the 1-octanol lamellae. Interpretation of the STM images suggests that the Moiré periodicity is governed by the electronic properties of the graphite surface and the 1-octanol layer periodicity.

1. Introduction

Engineering sophisticated organic nanostructures on surfaces has been the focus of recent research interest [1–3]. Controlling molecular self-assembly offers unique directions for the fabrication of two-dimensional (2D) supramolecular nanoarchitectures. The resulting structures can be tailored at the nanometer scale by exploiting molecule substrate [4, 5] or intermolecular interactions [1, 2]. Molecular shape, size, structure and substituents are key parameters driving the structure of self-assembled nanoarchitectures. The alkane molecule is a particularly attractive building block because its extremity can easily be functionalized to interact with other molecules or with the surface [6]. Numerous organic patterns resulting from modified-alkane self-assembled structures have been reported or predicted on graphite, graphene and other surfaces [7–10].

Different lamellar structures have been experimentally observed depending of the molecule arrangement and configuration. The axis of the molecule forming the lamellae can be aligned [8, 11] or rotated by an angle [12] that is usually governed by substrate geometry. It has also been observed that molecules can lie flat or perpendicular to the surface [10, 7]. Molecules can also adopt a straight or twisted configuration (cis or trans conformation) [13]. Racemic and enantiomer nanoarchitectures can be formed.

These structures can be exploited in nanotechnology as nanotemplates or active layers. For example, a substituted alkane derivative monolayer on graphene/SiO\textsubscript{2} has been successfully used to build a graphene field effect transistor dedicated to mercury detection [14]. Exploiting the formation of hydrogen bonds (H-bonds) between alkane derivative building blocks to create novel 2D structures is particularly appealing because of the strength [15] and the high selectivity and directionality of these bindings [16, 17]. It has been shown that single [18–21, 17] and multicomponent [22–30] self-assembled organic nanoarchitectures can be achieved through hydrogen bonding.

Thomas \textit{et al} observed using scanning tunneling microscopy at the solid/liquid interface that the self-assembled arachidic acid layer on graphite was creating a Moiré pattern in the STM image [31]. Nath \textit{et al} also observed Moiré patterns when a 1-heptadecanol-trimesic acid layer was formed on graphite [32]. In these two cases the Moiré pattern appears like a superstructure of hexagonally ordered bright spots that are \~2 nm large. Graphitic Moiré pattern phenomena have recently been the focus of intensive research interest because of their specific electronic properties [33–36].
This type of Moiré has been exploited as a two-dimensional template for creating an ordered, large scale assembly of molecules [34, 37, 38] and metal clusters [39]. In addition it has been observed that patterned adsorption of atomic hydrogen onto graphitic Moiré superlattice positions could modify honeycomb carbon layer electronic properties [38]. The ability to tailor the extremely sensitive carbon layer electronic properties through the formation of specific Moiré patterns is expected to lead to major developments in various applications, as ultra-sensitive strain gauges, pressure sensors or ultra-thin capacitors.

In this paper we investigate the self-assembly of 1-octanol molecules (CH$_3$(CH$_2$)$_7$OH) on graphite at the solid/liquid interface. Scanning tunneling microscopy (STM) shows that the molecules form a two-dimensional close-packed hydrogen-bonded chevron arrangement on the surface. STM images also reveal that a Moiré pattern appears when the 1-octanol layer is covering the graphite surface.

2. Experimental details

A droplet of 1-octanol solution (98%, Acros) was deposited on a freshly cleaved graphite substrate. The droplet spread and formed a thin liquid film on the surface. The STM imaging of the samples was performed at the liquid/solid interface 1 h after droplet deposition using a Pico-SPM (Molecular Imaging, Agilent Technology) scanning tunneling microscope. The surface appeared to be wet during STM acquisition. Cut Pt/Ir tips were used to obtain constant current images at room temperature with a bias voltage applied to the sample. STM images were processed and analyzed using the application FabViewer [40].

3. Results and discussion

The chemical structure of the 1-octanol molecule (CH$_3$(CH$_2$)$_7$OH) is presented in figure 1. This molecule is a straight chain fatty alcohol with eight carbon atoms. This linear molecule has a hydroxyl functional group (–OH) as head and an alkyl chain as tail. The (–OH) group is expected to give a notable polar effect to the molecule.

The large scale STM image in figure 2(a) reveals that 1-octanol forms large 2D nanoarchitectures at the liquid/graphite interface. STM images show that molecules self-assemble into a close-packed network. This structure is composed of organic lamellae, which are ∼2.1 nm large, figure 2(b). These lamellae are aligned in the (1000) graphite crystallographic direction. Large periodic bright stripes are visible in the STM images, figure 2. These stripes are almost perpendicular to the molecular lamellae, i.e. they are aligned in the (2100) graphite crystallographic direction. The stripe periodicity is ∼3.9 nm. This domain is coexisting on the surface with similar domains rotated by an angle of 60°.

A high resolution STM image of the 1-octanol network is presented in figure 3. Molecules appear flat-lying on the surface and densely packed. The image shows that the molecules are forming a herringbone structure. The angle between the molecules in the lamella and at the lamella boundary is 120°. Blue arrows in figure 3(a) indicate a tip change during STM image recording, revealing that the STM tip apex has been modified during the scan. STM tip apex modification is a powerful method used to enhance electronic contrast in STM images of nanostructured surfaces [41–45]. It is usually used to distinguish the electronic contribution from the surface morphology contribution in the STM image contrast. In figure 3(a) STM tip modification reveals that the integrated density of state in the center of the lamella is different from the lamella boundary, i.e. the lamella center appears bright whereas the lamella boundary appears dark.

We attribute this enhanced brightness in the lamella center to result from hydrogen bonding between molecular hydroxyl functional groups. This shows that molecules are preferentially arranged in head-to-head and tail-to-tail
sequence in the ⟨2100⟩ direction because a head-to-tail arrangement would lead to a similar density of states in the center and at the border of the lamella. The model representing the herringbone arrangement is shown in figure 3(b). In this model the 1-octanol arrangement is stabilized by double O⋯H–O hydrogen bonds between molecules; i.e. each molecule is connected to two neighboring ones through hydrogen bonds. These bonds are represented by dotted red lines in figure 3(b). The network unit cell is rectangular with ∼5.6 Å and ∼21.0 Å unit cell parameters. The molecular zigzag arrangement is the result of a flat orientation of the molecules caused by a series of CH-π interactions between the CH group of the alkyl chain and the π electron system of the graphite carbon surface [46].

Figure 4 shows a large scale STM image of the 1-octanol organic layer on graphite. In the right and bottom side of the figure, green and red rectangles have been superimposed on the STM image as a guide for the eyes, indicating the orientation of molecules in each network row. This image reveals that the angle between molecules of neighboring rows is generally 120°, except at the boundary indicated by the black arrow in figure 4. At this boundary, molecules are aligned in the same direction. This means that molecules are only locally arranged in a head-to-tail configuration.

The STM images show that 1-octanol molecules are self-assembled at the solid/liquid interface into a well-ordered organic monolayer, with molecules lying flat on the graphite surface. The organic monolayer consists in rows that are stabilized via side-by-side van der Waals interactions between the alkyl chains. The STM images show that the image contrast in the 1-octanol lamella center and at the lamella boundary is different. This therefore reveals that the molecules are not arranged in a head-to-tail fashion, which would lead to similar contrast. They are instead preferentially arranged alternately in a 120° head-to-head and 120° tail-to-tail fashion as represented in the model figure 3(b). The head-to-tail arrangement was only locally observed at the 1-octanol domain boundary when molecules of neighboring rows are aligned in the same direction (figure 4). The head-to-head structure is stabilized by double hydrogen bonds (2 O⋯H–O) between molecular hydroxyl functional groups. Ab initio calculations showed that this 120° binding leads to the formation of the most stable hydrogen-bonded arrangement in the case of long chain alcohols adsorbed on graphite or the graphene surface [7]. However, this structure differs from the self-assembled lamellar chevron network of 1-octadecanethiol [42], where molecules of neighboring lamellae are aligned at the lamellar
boundary (aligned tail-to-tail binding) whereas the angle is preferentially 120° in the case of 1-octanol, as observed in figures 3 and 4.

STM images also reveal that a Moiré pattern appears when the 1-octanol herringbone network is formed on the graphite surface. In the case of 1-octanol on graphite, the Moiré pattern consists of stripes aligned in the (2100) direction, perpendicular to the lamella direction. The Moiré pattern periodicity in the (1000) direction is ~3.9 nm. STM images show that this distance corresponds to seven 1-octanol unit cell parameters in the (1000) direction. Graphite unit cell periodicity in the (1000) direction is 2.46 Å. We will now discuss how the superposition of two layers having different periodicities can affect STM image contrast. Moiré pattern formation results from the superposition of two lattices having different unit cell parameters. An algebraic approach can be used to calculate the points of coincidence for these two lattices. The aim is to find a structural model for the 1-octanol adlayer and the graphite surface which is consistent with the distances and the translational symmetry seen in the STM images. The condition of coincidence of the two superposed lattices is governed by \((n \times \lambda_{ad}) = (n \pm 1) \times \lambda_{sub} = \lambda_{Moire}\), where \(\lambda_{sub}\) and \(\lambda_{Moire}\) denote the periodicity of the substrate surface, the 1-octanol adsorbed layer and the Moiré pattern in the (1000) direction. STM images show that \(\lambda_{Moire} \approx 3.9 \text{ nm}\), \(\lambda_{ad} \approx 5.6 \text{ Å}\) and \(n = 7\). This leads to \(\lambda_{sub} \approx 6.5 \text{ Å}\) (considering \(n - 1 = 6\)) or \(\lambda_{sub} \approx 4.88 \text{ Å}\) (considering \(n + 1 = 8\)). These distances are not in agreement with the graphite unit cell periodicity in the (1000) direction which is 2.461 Å. However, it should be noticed that the Moiré periodicity would fit a substrate periodicity that verifies 39 Å/8 = 4.88 Å. This value is very close to the double periodicity graphite in the (1000) direction that is 4.92 Å.

The graphite surface has been widely investigated using STM. It is well known that so-called atomically resolved STM images of graphite do not match the expected honeycomb structure of the material. There is still controversy about interpretation of the STM image of this surface [47]. It is generally admitted that STM images of graphite at the atomic scale display a hexagonal lattice where only half of the atoms are resolved. This is attributed to electronic effects [47–50] because surface neighboring carbon atoms are sitting in non-equivalent sites. One type of atom is sitting directly above the carbon atom of the underlying layer, whereas the second type of atom is located above the center of the carbon hexagon of the underlying layer. This results in the variation of the density of state of the graphite top layer due to interlayer electronic coupling. The structure observed using STM corresponds to a hexagonal network, whose periodicity is twice that of graphite (4.92 Å). It therefore appears that the Moiré pattern observed in the STM images presented in figures 2 and 3 corresponds to the point coincident between the 1-octanol layer and the electronic periodicity of the graphite surface in the (1000) direction. This suggest that the contrast in the STM image corresponding to the Moiré pattern has an electronic origin resulting from the coupling of the 1-octanol layer with the graphite surface. This effect has been mentioned by Ilan et al, who calculated that electronic coupling between the alkane and graphite surface could drastically affect the appearance of individual alkane molecules in STM images [51]. Our experimental observations show that STM tip modification can drastically enhance the amplitude of the Moiré structure in the STM image, as seen in figure 3. This also indicates that this Moiré structure results from electronic coupling between the organic layer and the graphite surface. New theoretical development and calculations are required to assess the interface interaction and the electronic coupling between the 1-octanol layer and the graphite surface.

4. Conclusion

In conclusion, scanning tunneling microscopy showed that 1-octanol molecules self-assembled into a herringbone structure on graphite at the liquid/solid interface. This organic architecture is stabilized by hydrogen bonds. STM images also reveal that a Moiré pattern appears when the 1-octanol herringbone network is formed onto the graphite surface. The Moiré periodicity corresponds to the point coincident between the organic layer adlayer and twice the periodicity of the graphite surface, which corresponds to the electronic periodicity of the graphite surface. This suggests that the Moiré pattern has an electronic origin. This technique opens new opportunities to tailor the structure of graphite and graphene surfaces using layers of functionalized alkane chains having different lengths in order to modify surface electronic properties for new developments in applications, as ultra-sensitive strain gauges, pressure sensors or ultra-thin capacitors.

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