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► **To cite this version:**

Fabien Silly. Moiré pattern induced by the electronic coupling between 1-octanol self-assembled monolayers and graphite surface. *Nanotechnology*, 2012, 23, pp.225603. 10.1088/0957-4484/23/22/225603 . cea-00837972

HAL Id: cea-00837972

<https://cea.hal.science/cea-00837972>

Submitted on 24 Jun 2013

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Moiré pattern induced by the electronic coupling between 1-Octanol self-assembled monolayer and graphite surface

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Abstract. Two-dimensional self-assembly of 1-Octanol molecules on 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 is the focus of recent research interest [1, 2, 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. 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, 8, 9, 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 [11, 12] or rotated by an angle [13] that is usually governed by substrate geometry. It has also been observed that molecules can lay flat or perpendicular to the surface [10, 7]. Molecules can also adopt a straight or twisted configuration (cis or trans conformation) [14]. Racemic and enantiomer nanoarchitectures can be formed.

These structures can be exploited in nanotechnology as nanotemplate or active layer. For example substituted alkane derivative monolayer on graphene/SiO₂ has been successfully used to build a graphene field effect transistors dedicated to mercury detection [15]. 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 [16] and the high selectivity and directionality of these bindings [17, 18]. It has been shown that single [19, 20, 21, 22, 18] and multicomponent [23, 24, 25, 26, 27, 28, 29, 30, 31] self-assembled organic nanoarchitectures can be achieved through hydrogen bonding.

Thomas *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 [32]. Nath *et al.* also observed Moiré pattern when a 1-heptadecanol-trimesic acid layer was formed on graphite [33]. 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 [34, 35, 36, 37]. This type of Moiré has been exploited as two-dimensional templates for creating ordered, large-scale assembly of molecules [35, 38, 39] and metal clusters [40]. In addition it has been observed that patterned adsorption of atomic hydrogen onto graphitic Moiré superlattice positions could modify honeycomb carbon layer electronic properties [39]. 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 (CH₃(CH₂)₇OH) 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.

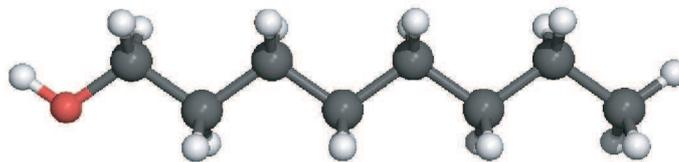


Figure 1. Scheme of 1-Octanol molecule ($\text{CH}_3(\text{CH}_2)_7\text{OH}$). Carbon atoms are gray, hydrogen atoms white and oxygen atom is red, respectively.

2. Experimental

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 1h 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 [41].

3. Results and Discussion

The chemical structure of 1-Octanol molecule ($\text{CH}_3(\text{CH}_2)_7\text{OH}$) 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 2a reveals 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 2b. These lamellae are aligned in the $\langle 1000 \rangle$ 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 $\langle 2100 \rangle$ 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 3a indicate a tip change during STM image recording, revealing that STM tip apex has been modified during the scan. STM tip apex modification is a powerful method used to enhance electronic contrast in

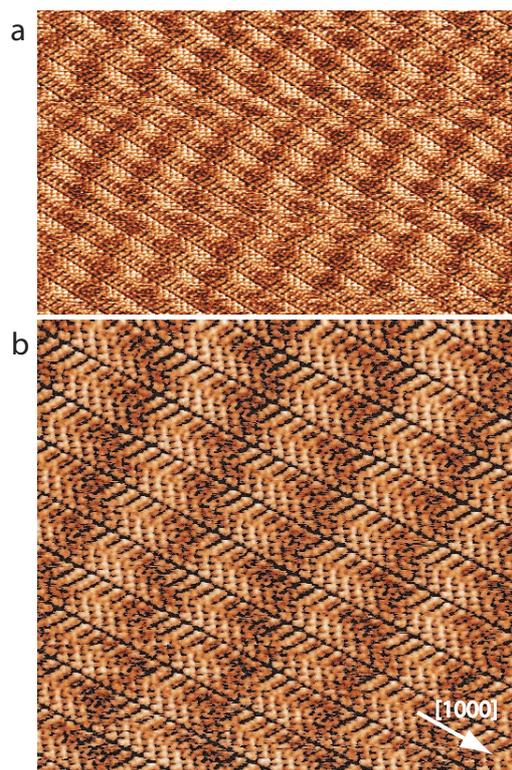


Figure 2. STM image of 1-Octanol self-assembled structures on graphite (a) $35 \times 22 \text{ nm}^2$; $V_s = 0.8 \text{ V}$, $I_t = 14 \text{ pA}$, (b) $17 \times 17 \text{ nm}^2$; $V_s = 0.8 \text{ V}$, $I_t = 14 \text{ pA}$. The [1000] graphite crystallographic direction is indicated by a white arrow.

STM images of nanostructured surfaces [42, 43, 44, 45, 46]. It is usually used to distinguish electronic contribution from surface morphology contribution in the STM image contrast. In Figure 3a STM tip modification reveals that the integrated density of state in the center of the lamella is different from the lamella boundary, i.e. lamella center appears bright whereas lamella boundary appears dark.

We attribute this enhanced brightness in lamella center to result from hydrogen bonding between molecular hydroxyl functional group. This shows that molecules are preferentially arranged in head-to-head and tail-to-tail sequence in the $\langle 2100 \rangle$ direction because a head-to-tail arrangement would lead to similar density of state in the center and at the border of the lamella. The model representing the herringbone arrangement is shown in Figure 3b. In this model the 1-Octanol arrangement is stabilized by double $\text{O} \cdots \text{H}-\text{O}$ hydrogen bonds between molecules; i.e. each molecule is connected to two neighbor ones through hydrogen bonds. These bonds are represented by dotted red lines in Figure 3b. The network unit cell is rectangular with $\sim 5.6 \text{ \AA}$ and $\sim 20.0 \text{ \AA}$ unit cell parameters. The molecular zigzag arrangement is the result of a flat orientation of the molecules caused by a series of $\text{CH}-\pi$ interactions between the CH group of the alkyl chain and the π electron system of the graphite carbon surface [47].

Figure 4 shows an large scale STM image of 1-Octanol organic layer on graphite. In the right and bottom side of the Figure, green and red rectangles have been superimposed

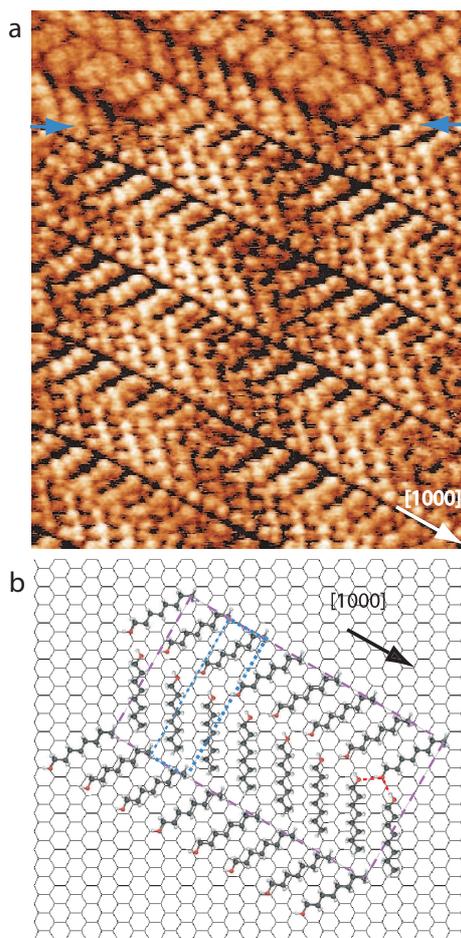


Figure 3. (a) High resolution STM image of 1-octanol structure, $10 \times 8 \text{ nm}^2$; $V_s = 0.78 \text{ V}$, $I_t = 14 \text{ pA}$, (b) Model of the 1-Octanol network. The network unit cell is represented by the dashed blue rectangle. Red dotted lines represent molecular hydrogen bond, the blue dotted rectangle represents the organic layer unit cell and the purple dotted rectangle represents the Moiré unit cell.

to 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 row 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.

STM images are showing that 1-Octanol molecules are self-assembly 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. STM images are showing 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 alternatively in a 120° head-to-head and 120° tail-to-tail fashion as represented in the model Figure 3b. The head-to-tail arrangement was only locally observed at 1-Octanol domain boundary when molecule of neighboring



Figure 4. STM image of 1-Octanol herringbone network boundary, $15 \times 15 \text{ nm}^2$; $V_s = 0.78 \text{ V}$, $I_t = 14 \text{ pA}$. Green (red) blocks are indicating the orientation of the molecule in each organic rows, respectively. The black arrow indicated the boundary separating two organic rows where molecules are oriented in the same direction.

rows are aligned in the same direction (Figure 4). The head-to-head structure is stabilized by double hydrogen-bonds ($2 \times \text{O} \cdots \text{H}-\text{O}$) 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 graphene surface [7]. However this structure differs from the self-assembled lamellar chevron network of 1-Octadecanethiol [43], 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 Figure 3 and Figure 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 in stripes aligned in the $\langle 2100 \rangle$ direction, perpendicular to the lamella direction. The Moiré pattern periodicity in the $\langle 1000 \rangle$ direction is $\sim 3.9 \text{ nm}$. STM images show that this distance corresponds to 7 1-Octanol unit cell parameter in the $\langle 1000 \rangle$ direction. Graphite unit cell periodicity in the $\langle 1000 \rangle$ direction is 2.46 \AA . 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 $(n \times \lambda_{ad}) = (n \pm 1) \times \lambda_{sub} = \lambda_{Moiré}$, where λ_{sub} , λ_{ad} and $\lambda_{Moiré}$ denote the periodicity of the substrate surface, the 1-Octanol adsorbed layer and the Moiré pattern in the $\langle 1000 \rangle$ direction. STM images show that $\lambda_{Moiré} \simeq 3.9 \text{ nm}$, $\lambda_{ad} \simeq 5.6 \text{ \AA}$ and $n = 7$. This leads to $\lambda_{sub} \simeq 6.5 \text{ \AA}$ (considering $n - 1 = 6$) or $\lambda_{sub} \simeq 4.88 \text{ \AA}$ (considering $n + 1 = 8$). These distances are not in agreement with the graphite unit cell periodicity in the $\langle 1000 \rangle$

direction which is 2.461 Å. However it should be noticed that the Moiré periodicity would fit a substrate periodicity that verifies $39 \text{ Å} / 8 = 4.88 \text{ Å}$. This value is very close to the double periodicity graphite in the $\langle 1000 \rangle$ direction that is 4.92 Å.

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 [48]. 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 [48, 49, 50, 51] because surface neighboring carbon atoms are sitting in non-equivalent sites. One type of atom is sitting directly above carbon atom of the underlying layer, whereas the second type of atom is located above the center of 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 the one of graphite (4.92 Å). It therefore appears that the Moiré pattern observed in the STM images presented in Figure 2 and Figure 3 corresponds to the point coincidence between the 1-Octanol layer and the electronic periodicity of the graphite surface in the $\langle 1000 \rangle$ direction. This suggests 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 alkane and graphite surface could drastically affect the appearance of individual alkane molecules in STM images [52]. 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 is also supporting 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 coincidence 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 length in order to modify surface electronic properties for new developments in applications, as ultra-sensitive strain gauges, pressure sensors or ultra-thin capacitors.

Acknowledgments

The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP7/2007-2013) / ERC grant agreement n° 259297.

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