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Final Paper

Examination of Molecular Self-Assembly with Scanning Tunneling Microscopy

Abstract

Substrates like graphite and gold are imaged with and without molecular adsorbates such as alkanes and alcohols. Imaging conditions, e.g, solvent and the ambient surroundings are changed. We investigate the structures and dynamic properties of these systems. Our objective is to learn how to manipulate variables, such as functional groups, electric fields, and adsorbate-substrate interactions, to control self-assembly. We focus mainly on imaging surfactants on Highly Oriented Pyrolytic Graphite and Au (111) surfaces. These self-organized molecular systems can provide templates for nano-wire designs.

1. Introduction

I. Motivation

Many molecules can self-assemble into sophisticated structures on a surface. These structures have potential value in the development of nanotechnology. Understanding and controlling molecular arrangements on a surface is imperative if we wish to turn these molecules into nanometer scale sensors and computational devices. Scanning Probe Microscopies, such as Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM) constitute a powerful approach in elucidating nanometer scale phenomena on surfaces. Scanning Tunneling Microscopy is capable of "visualizing" atoms and molecules. It offers an invaluable way of elucidating the molecular interactions that control self-assembly at interfaces. Equipped with such information we could control such self-assembly, a process that may be potentially influential to nano-

technological advances. Though the technology of Scanning Tunneling Microscopy (STM) has been available for many years ⁽¹⁾, many phenomena remain somewhat puzzling. Even STM images of simple systems, such as highly oriented pyrolytic graphite (HOPG), elude our complete comprehension.

Equipment: The Scanning Tunneling Microscope

The Scanning Tunneling Microscope's most crucial feature is an atomically sharp wire that acts as a "tip," detecting electrical current when a bias is applied between the tip and a conductive substrate. This current flow is due to the high probability of quantum tunneling electrons between the tip and the substrate when the tip is at a distance of about 1 nanometer or less from a conductive surface. Quantum tunneling is the property that all particles have a small, but finite probability of "tunneling" (moving from one side of a potential barrier to another without any damage to the barrier). This probability depends exponentially on particle mass, barrier height and thickness. The formula for quantum tunneling is shown below

$$I = I_0 e^{-\sqrt{\frac{8m\varphi}{\hbar^2}}S}$$

Formula 1: the barrier height, $\boldsymbol{\phi}$ is related to the current, I, and distance, S through this formula

As is appreciable from the equation, the probability of tunneling is negligible except for extremely light particles, across extremely thin potential barriers. Electrons traveling a distance of a few angstroms fulfill such requirements of mass and distance, and therefore there is a finite probability for electrons to tunnel through the tip-sample gap.

A piezoelectric ceramic, which expands and contracts with applied voltage, controls the position of the STM tip. The computer driven piezo scans tip across the surface and records the tunneling current at each point on the surface to create an image. Our Scanning Tunneling Microscope can scan at speeds from 0.1 to 25.7 lines per second. Generally higher speeds are used for small scanning areas. Scanning large areas with high speeds will not give the STM tip as accurate information about the surface beneath it; it does not have ample time to collect and evaluate tunneling current data. Conversely, scanning small areas with an extremely slow speed will make thermal drift an issue, as the sample is moving faster than the tip has time collect data on that area. Generally, keeping the scanning pace to between 1000 nm/s and 3000 nm/s will produce good results, adjusting as needed. A diagram of the experimental setup for electrochemical STM is shown below.

Experimental technique: In-situ Electrochemical STM



RE:Reference electrode

Diagram 1

Illustration of the STM: An illustration of the STM experimental setup for under electrolyte solution. The most crucial features are the atomically sharp tip, the piezo-electric and the reference (RE) and counter electrodes(CE).

Scanning Tunneling Microscopy can be performed in air or under an electrolyte solution. When scanning in air it is necessary to attach the sample plate to the bottom of the Scanning Tunneling Microscope and plug the microscope wires into the sample plate. After this, the sample can be approached to the tip using the STM computer controls

In a conductive solvent, e.g. an electrolyte, some of the electrical current detected by the microscope may not due to electrons tunneling to or from the surface. This so-called leakage current must be minimized for optimal STM imaging. This is achieved by minimizing the exposed area of the STM tip, and setting the tip potential so that the current, when withdrawn from the surface, but surrounded by electrolyte, is at a minimum; raising or lowering the potential increases the current. Minimizing the exposed area of the tip is accomplished through polyethylene or wax coating, as discussed below in *Producing STM Tips*.

Under an electrochemical environment, the sample voltage as well as the tip potential must be controlled independently with respect to a reference electrode. The electrolytic solution must also be extremely pure, or else it contaminates the sample. The electrolyte must be contained in a Teflon cell of which the sample acts as a base. This cell is cleaned successively with piranha (2 parts H_2SO_4 , and 1 part H_2O_2) and nitric acid each for 30 minutes. It is rinsed with deionized (DI) water to assure that no contamination of the sample has occurred. Two electrodes, a reference electrode and a counter electrode, are placed in the cell. They are connected so that the reference electrode can serve as a potential reference to both the tip and the sample. To avoid short-circuit, the electrodes should not touch either each other or the sample.

The Scanning Tunneling Microscope can be operated in two modes- current and topographic. In Current mode, the microscope scans the tip across the surface while keeping constant Z height and records the tunneling current as a function of sample X and Y position. In topographic (also called constant current mode) mode, the microscope adjusts the tip-sample position to keep the tunneling current constant. The advantage of working at topographic mode is that there is a smaller chance that tip might accidentally crash, or hit the surface. However, current mode typically produces more detailed images and can contain information the electron density of the surface.

Producing STM tips

Tungsten tips are made by etching in 3 M potassium hydroxide. The tip etching setup is shown below. A 0.25 mm tungsten wire is threaded through a platinum-iridium wire loop. The loop is filled with KOH (3.0 M) and a small AC Voltage (1-5V) is applied between the loop and the wire. The potassium hydroxide etches the tungsten wire and a small "neck" forms in the wire. This etching continues until the neck is so thin that the weight of the lower-neck wire causes the lower portion of the tip to fall. This fallen etched part of the wire becomes the scanning tunneling microscope tip.



Diagram 2

Tungsten Tip etching: a simple illustration of wire etching. The blue fluid represents the potassium hydroxide. The small cup below will catch the lower tip and a potential of roughly 1-5 V is carried through the wire and loop, making a closed circuit when the potassium hydroxide is present. Closer examination shows neck is formed where the potassium hydroxide meets the wire.

Tungsten tips are usually used for imaging under electrolyte. They are coated either in wax or polyethylene. The procedure for coating in wax is as follows. It is dipped in hot wax, with a temperature approximately 77 degrees centigrade, 1-3 times. This is to ensure that during electrochemical imaging, when the tip is immersed in solution, the leakage current is minimized. That the objective is an entire tip well coated in wax save the atomically sharp end, which is must be uncoated in order to read tunneling current.

In some circumstances wax is not appropriate. For example, when imaging in surfactant solutions the leakage current was observed to increase due to dissolution of wax by surfactant. In such cases a Polyethylene coating was applied to the tip. This requires the extra equipment shown in Diagram 3. A small copper plate is attached to the end of a soldering iron. This plate has a U-shape design, which allows the tip to move to the center of the plate. (Inner part of the U) A temperature control unit is used to monitor and control the temperature of the copper plate. We use a temperature of roughly 168 °C. After the temperature has stabilized, a polyethylene tablet is melted atop of the hot copper plate such that it covers the indent in the plate. The tungsten tip is positioned and pushed through the melted polyethylene in the middle of the plate from below. It is then taken away from the hotplate, through U-shaped slit. When the tips it cools a hard polyethylene coating forms. The speed one moves the tip through the polyethylene and the temperature of the hotplate both affect how well the tip is coated. Too cool or fast may leave the tip undercoated, whereas too hot or slow may leave it overcoated. Typically, for both wax and polyethylene coatings a well-coated tip will read a current of 0.01 nA or less when in optimal voltage conditions. (This varies with the tip potential. Current as a function of potential is a parabolic curve. The voltage under which a tungsten tip has minimum current is about $0V_{SCE}$).





Platinum-Iridium tips are made by simultaneously pulling and clipping a piece of platinum-Iridium wire. Because of the properties of platinum, this simple method is as

effective as etching in producing atomically sharp tips. Tungsten tips cannot be made in this way because this method produces flat ends on tungsten. However, platinum iridium breaks with many edges that are atomically sharp. Generally, these tips are used for Scanning Tunneling Microscopy in air. Since air is not very conductive in this situation, no coating is necessary, therefore they are not coated.

This paper is divided into two main topics. The first topic is that of the symmetry of highly oriented pyrolytic graphite. The second is that of controlling molecular selfassembly at interfaces. Each topic is divided into Hypothesis, Preparation, Results and Conclusion.

II. <u>The Symmetry In STM images of Highly Oriented Pyrolytic</u> <u>Graphite</u>

1. Hypothesis

Highly Oriented Pyrolytic Graphite (HOPG) is one of the simplest surfaces to image using Scanning Tunneling Microscopy (STM). Its layered structure holds special properties, such as flatness, stability in air, and the ability to cleave into clean surfaces, which make it attractive for simple STM imaging. However, even this simple, commonly imaged surface, defies our complete comprehension.⁽³⁾ Typically, STM images of HOPG reveal a six-fold or hexagonal symmetry, where six similar bright spots surround every bright spot. ⁽⁴⁾ HOPG is known to have honeycomb symmetry, contrary to STM images; its true structure cannot be as the images suggest. The known distance between atoms in HOPG, 1.4 Å, is also not consistent with STM images. STM images usually suggest distances of about 2.4 Å between features. As shown in figure 3, a hexagonal symmetry could result if only half the atoms were being imaged. If all the atoms were image then threefold symmetry would be apparent.

Typically, one obtains an image of bright spots where there is a small connection, if any between the spots (Fig 2) . VonToussaint, Schimmel and Kuppers ⁽⁵⁾ relate such observations in Atomic Force Microscopy (AFM) to elastic tip-sample interactions. That is, the HOPG surface and the Scanning Tunneling Microscope tip are electrically interacting slightly with each other, attracting more in some spots and less in others. Lee et. al. ⁽⁶⁾ used Hartree-Fock calculations to predict similarly. Atamny et. al.⁽⁴⁾ proposed that Scanning Tunneling Microscopy imaged the inverse of the apparent structure of graphite, imaging the center of a carbon ring, rather than the individual atoms.

Both the theoretical explanations of Atamny et. al. and Vonussaint et. al rely on the assumption that not all graphite atoms on a surface layer are equal. Generally, the consensus is that in STM imaging this due to inequivalence in so-called A and B site atoms, where A-site atoms represent those directly over an atom in an underlying layer and B-site atoms refer to those unencumbered by such interactions. (So-called H site atoms represent lower layer atoms that do not reinforce imaging as b-site atoms are hypothesized to. These atoms correspond to the placement of the "hollow" referred to by Atamny et. al, however it has never been suggested that these atoms are actually imaged because they are located in the lower layer of graphite) A-site atoms either experience a lower electron-density state due to their interactions with the underlying layer or are dimensionally lower or both, This exponentially lowers it's the ability to of electrons to or from A to tunnel across the potential barrier and be read as current by the STM. It is therefore assumed that graphite layers, rather than being directly on top of one another are at opposing places. In other words, the center of the carbon rings do not align with each other. (If you were to draw a line through the middle of carbon rings in successive layers of graphite, the line would not be normal to the surface, but rather at an angle) This is called ABAB symmetry.

Studies have been performed involving one graphite layer on Pt (111). ⁽⁷⁾ Since only one layer of graphite is involved A and B site structural asymmetry should be removed. However, the studies ⁽⁷⁾ found that still only three of the six atoms in a carbon ring were being imaged. This was attributed by Tchougreeff and Hoffman⁽⁸⁾ to electron-electron

interactions within a single layer. Specifically, electron transfer between A and B site atoms, and the attraction and repulsion of electrons in various similar or adjacent states (Charge Density and Spin density wave considerations) and their attraction to the core of adjacent atoms were held responsible. However this last theory was disproved by Whangbo et. al. ⁽⁹⁾, who extended the considerations of Tchougreeff and Hoffmann and showed that asymmetry of graphite should be (by those considerations) dependant on the polarity. This did not agree with experimental findings, and thus they ⁽⁹⁾ theorized that the asymmetry is not caused by charge density or spin density waves. He theorized that B-site atoms were more compressed than A-site atoms, which was causing the asymmetry observed.

Despite the various theories on why the common image of graphite was so decisively different than its actual structure, previous groups have been able to obtain images where all atoms have been imaged. This is normally attributed to small?? Translation movements in the overlaying layer of graphite, caused by the movement?? of the Scanning Tunneling Microscope tip. ⁽¹⁰⁾ Diagrams 4 and 5 model two possible layer formations of graphite. Bright dots indicate those atoms thought to be imaged in each case. Diagram 4 displays two graphite layers one atop of the other with ABAB stacking and the atoms thought to be imaged whereas diagram 5 displays seemingly one graphite layer, but actually two, directly atop off one another and the atoms thought to be imaged.



FIGURES OF THEORETICAL GRAPHITE STRUCTURE. Diagram 4 models a normal ABAB formation of graphite. Diagram 5 is a model of imaged graphite. Circles represent imaged regions. From diagram 4 to diagram 5, the distance between such regions goes from 2.4 Å to 1.4 Å. This change in distance correlates with going from imaging every other atom to every atom.

2. Sample Preparation

We obtained a clean sample surface by cleaving the with scotch tape. This is simply done by placing the tape on the graphite and pulling a thin layer of graphite off of the sample. This is usually repeated 6-10 times or more, to help ensure that the surface to be imaged is free from extraneous debris. This peeling can be performed because graphite layers interact weakly and are easy to pull apart. Interactions between C atoms in each plane are strong, but between C atoms in different planes are weak.

Our tips are made of 0.25 mm diameter platinum-iridium wire. The wire was cut as aforementioned above in *Producing STM Tips*. As is usual with platinum-iridium tips, the HOPG sample was imaged in air in topographic mode

3. *Results*

Our group previously took Images of HOPG this summer, which displayed complete honeycomb structure. These images are shown below as figures 1 and 2. Figure 3 is an example of commonly seen images of graphite. The distance between each bright spot in Fig 1 is roughly 1.4 Angstroms. Distances between suspected atoms are consistent with proposed distances between carbon atoms.(1.4A) This is consistent with a situation where surface and underlying graphite layers align. However, it may be due to changed imaging parameters or conditions. The bias voltage was maintained around 0.1 V, current at 0.1 nA. Imaging speed seemed to have no affect on both threefold and sixfold patterns in image. They stayed consistently as either one pattern or the other, unlike previous reports. The images were extremely stable and did not appear to be dissipating at any rate, in contrast to previous three-fold symmetry images that fluctuated with time (3) In addition, no higher, super-symmetry images within the graphite occur. (A common occurrence in imaging graphite with sub-layers at angles less than 60° from the imaged layer) This distinguishes these images from such Moiré patterns, such as figure 4, 5 and 6 or other similar phenomena.

Moiré patterns are the result of two layers of graphite at a slight angle with one another. (Diagram 6) This slight shift produces a larger than atomic scale six-fold symmetry, as the layers move from being in phase to out of phase with each other. That is, at some places, their atomic symmetry is in step and in others it is out of step. In step correlations amplify the tunneling current, making the image brighter in those regions. If ABAB symmetry is responsible for six-fold atomic symmetry, at these points, the atomic symmetry should be three-fold, as the two layers of graphite are nearly exactly on top of one another. As the image progresses away from these in step regions, the image should get darker and the three-fold symmetry should turn to six-fold, as the two atomic layers become decoherent. The angle by which two layers are offset is not large. In diagram 6, the theoretical offset between the two layers is roughly 7 degrees.



Moire patterns of graphite made by two layers of graphite: A computer rendition of two graphite layers overlapping to create Moiré patterns. A change in angle of merely 7° can produce large super symmetry patterns. The smaller the angle between layers, the bigger the periodicity of the super symmetry.

Changing bias and current parameters will test our hypothesis of graphite layer orientation. Ideally one wants to find and image an atomically sharp step, in hope of imaging both surface and underlying graphite layers and observing their relative orientation, and displacements. If, B-site and A-site atoms correspond to their proposed positions, it can be assumed that layer interactions are responsible for different HOPG images. Our next step would be to discover and use methods to control and manipulate layer-layer interactions in hope of understanding such interactions more thoroughly. That is, we wish to be able to control the movements of one layer upon another. In this way we can move the layer and track the corresponding change in image. If the symmetry of the images change, we have reason to believe that layer-layer interactions are responsible for symmetry, as they would be the only other parameter to change. If the symmetry of HOPG does not change, then we can assume that this STM phenomenon of producing an image that does not correspond to the surface structure of graphite is due to some other property of graphite.







Image dsiplaying three-fold symmetry graphite. Fig. 1 shows a clear image of this three-fold symmetry. The bright hexagonal pattern is a computer representation of STM data. This hexagonal structure compares favorably with the actual structure of HOPG. Fig 2 displays a large zoomed out version of the same phenomena. Although distinct atoms are not distinguishable, one can tell this patter is continuous throughout a large region with no super-symmetry pattern distorting it.





Bias= 0.05\

Scanned 1 -

Fig 4

Fig 3



Image examples of six fold or non-consistent Three Fold Symmetry. Fig 3 is an example of six-fold symmetry. Each bright spot portrayed by the computer corresponds to a skip-atom approach, where the distance, 2.4 A is the distance between an atom and an atom a third of the distance of a carbon ring. Fig. 4 is an example of Moiré super-symmetry. The six-fold periodicity (roughly 55 Å) is too big to be of the atomic scale Fig. 5: a closer image of the six-fold symmetry reveals another underlying symmetry at the atomic scale. 6: The hexagonal pattern corresponds to that of graphite, whereas bigger bright spots are attributed to layer rotation super-symmetry. One notices that the graphite structure is broader in such dark spots and more condensed in bright spots.

4. Conclusion

Images of HOPG, displaying three-fold and six-fold symmetry, have been obtained. These images were sustainable (i.e. They were not a function of time) and correlated with the length scale and structure atomic resolution images of Highly Oriented Pyrolytic Graphite. Conclusive evidence on whether this was due to imaging conditions or the state of the graphite surface has yet to be determined. Preliminary results suggest that these images were independent of imaging conditions.

Although many theories have been presented in the literature to explain the threefold and six fold symmetry, no theory appears to explain the phenomena. If it is the center of the carbon rings that is imaged as bright spots, then ABAB layer stacking

cannot be to blame because the atoms are not being imaged at all. In this theory, all atoms are treated equally, with the center of the carbon rings being the anomaly. If ABAB symmetry were responsible for the apparent six fold symmetry imaged by STM, then the "hollows" could not still be imaged and STM maintain six-fold symmetry; A atoms and hollows would be imaged and the resulting image would be of two six-fold symmetry patterns slightly askew from one another. Explanations on why three-fold symmetry is sometimes apparent must be presented. If ABAB stacking is responsible, then why do inverse images of six-fold symmetry images reflect graphite structure? Mathematical constructs and simulations appear to give different results and although ABAB stacking is the most common theory, it does not fully explain how continuous three-fold symmetry should appear except by luck. There is still much to be learned about this simple systems like HOPG, we must be extremely wary of how we interpret more complicated systems

I. <u>Controlling Molecular Self Assembly at Interfaces</u>

1. Hypothesis

The ability to control molecular self-assembly has the potential of facilitating the production of nano-computational devices through processes like template directed electro-deposition of metals to produce nano wires; in order for electro deposition to produce nano-wires, one needs to deposit the metal into some kind of template in which to mold or guide the formation of wires. Self-assembled molecular rows can serve as such a template, creating crevices in which metal can be deposited. Since the structure of self-assembly in these surfactants guides the creation of nano-wires, it is imperative that such structures are well ordered, creating the wires that are small, long, straight and unattached to any other forming wire. Control over the self-assembly of molecules is therefore a key component in creating functional nano-wires. Two surfactants that have suitable for ⁽¹⁵⁾ creating nanoscale templates are Sodium Dodecyl Sulfate (SDS) and Cetyltrimethylammonium hydrogensulfate (CTAS). We are interested in the factors that

control the self-assembly of these molecules, including molarity, voltage, and time dependence. Although it is well known that SDS and CTAS create well-ordered self-assembled mono-layers, it is our interest to find out what and how environmental factors manipulate self-assembly.

SDS nano-wire templates have successfully been made on numerous occasions. Wanless et al. have imaged SDS on HOPG with ⁽¹⁶⁾ and without ⁽¹⁷⁾ divalent ions with Atomic Force Microscopy (AFM). Divalent ions (in this case Mg²⁺, Mn²⁺ and Ca²⁺) are anticipated to alter the electrostatic interactions between charged headgroups on Sodium Dodecyl Sulfate. This is supposed to change the structure of the monovalent ions. Wanless, however, found that the adsorbed structures are similar to those imaged with just monovalent counter ions in the solution. The periodicity of the SDS hemi cylinders decreased linearly when a low concentration SDS included Mn²⁺ and Mg²⁺, where Mg²⁺ appeared to have a limiting diameter. Without divalent ions, .⁽¹⁶⁾ SDS adsorbed to the graphite-solution interface at concentrations of 2.8-81 mM. NaCl and SDS concentrations decreased the period of the hemi cylinders. In NaCl solutions, the period is roughly equal to the solution DeBye length.

Other groups have imaged SDS on metal surfaces like Au (111). Burgess et. al. ⁽¹⁸⁾ imaged a thin SDS film at the Au (111) electrode surface. They found that the SDS molecules self-assembled into long-range two-dimensional lattices with dimensions 4.4 and 0.5 nm. These lattices were at a 70° angle. Burgess et. al.⁽¹⁸⁾ hypothesized that the SDS two dimensional lattice consisted of two SDS molecules stretched along the longer dimension, with inward facing hydrocarbon tails. The rest of the SDS molecules in the hemimicelle are assumed to have a tilted orientation. The structure's stability comes from its interactions with the sulfate groups of adjacent cells. ⁽¹⁸⁾ The transition of SDS cells from a condensed state is thought to be reversible by variations in electrode potential.

Experiments ⁽¹⁹⁾ concerning Sodium Dodecyl Sulfate and Au(111) have also been conducted under electrolytes, such as HClO₄. Tang et. al. ⁽¹⁹⁾ observed in situ Scanning

Tunneling Microscopy the adsorption of SDS on Au (111) under potential control. The STM images revealed that SDS changes from a hemi-cylindrical micellar monolayer to a compact and uniform bilayer through potential control. This transition turned out to be irreversible with time. This is considered the model of potential-induced transformations for SDS aggregates on Au (111).

In order to properly understand and deposit SDS on a surface, we have worked with many different surfactants on HOPG and Au (111) surfaces including 8CB liquid crystal ⁽²⁰⁾ and eicosanol. ⁽²¹⁾ Both of these surfactants are regularly used in understanding self-assembly on surfaces. HOPG and Au(111) are commonly used surfaces concerning templates and nano-wires.

2. Sample Preparation

Au (111) was cleaned by sonicating for 10 minutes in Deionized water, and soaking in piranha solution (2 $H_2SO_4/1 H_2O_2$) for 30 minutes to an hour. After that, it is rinsed and sonicated again in DI water for 10 minutes. We then leave it in a Nitric Acid solution for 30 minutes to an hour. Then we rinse in DI water and sonicate twice for ten minutes. Finally we flame anneal the crystal using a hydrogen flame, for five minutes. It is immediately covered in Argon gas and allowed to cool. While under Argon gas, we prepare the STM setup, minimizing the crystal's time in air, where it could be contaminated. This intense cleaning process is required to reduce contamination on the crystal. It is imperative that the surface of the crystal be extremely clean. We work under HClO₄, perchloric acid to eliminate more surrounding interference under potential control. A program named Pico scan 5 controls the PicoSTM system (Molecular Imaging). The graphite (HOPG) used in this experiment is cleaned by as described before.

SDS was applied to graphite surfaces with a pipette, either by releasing a small droplet and allowing time to evaporate it into a thin film or by blowing bubbles through the pippetter and applying a thin film with the bubble, allowing for instant scanning.

Under electrolyte, SDS was added into the electrolyte either directly in the cell or in a clean beaker then poured into the cell. The concentration of SDS is lowered by the presence of electrolyte.

Other surfactants like 8CB liquid crystal and eicosanol were applied to graphite using a pipette as before. A drop was left on the graphite and spread into a thin film after cleaving.

3. Results

Preliminary results show, graphite surfaces prove easier to image or produce selfassembly than Au (111). There were difficulties in using wax-coated tips to image under surfactants. It was observed that the leakage current would increase in time while nonsurfactant substances were displaced on the surface. It is hypothesized, since the CMC of the solution is lowered when SDS is introduced, the wax on the tip dissolves, depositing wax on the Au (111) surface and creating a greater leakage current from the tip. Two approaches were taken. Firstly, we reduced the concentration of SDS to see the effect on the wax tips. Secondly, we used a kind of polymer coating that would not dissolve so easily. Other molecules were imaged while these problems were being solved

Images of HOPG with adsorbed 8CB liquid crystal molecules are shown below. 8CB molecules consist of two benzene rings, a long alkane chain and a functional group. They display incredible amounts of self-assembly, creating continuous straight rows without any interference from the STM. Each picture is an example of a different way 8CB can self-assemble into ordered monolayers. These images simulate the results we wish to achieve with SDS on both HOPG and Au(111). Molecular resolution gives us an idea of the structure of the 8CB molecules in each situation. As is apparent, each image displays a different molecular structure; therefore various hypothetical structures must be conceived to accommodate each image. The many different structures apparent suggest that there are more than one way for a molecule to self-assemble. Figure 6, 7, and 8 present patterns of self-assembly for which the molecular structure has not been

determined. Figure 5 and 7 are possibly two different views of the same self-assembled pattern, however we are not yet sure. It looks almost as if the rows of self-assembly in figure 7 are assembled above many other rows of self-assembly. Previous groups have found the pattern represented in figure six. ⁽²⁰⁾



8CB liquid crystal molecule on graphite. Fig 5-8 displays different self-assembled rows with different molecular structures. The molecular assembly of Fig. 5 is shown below. Similar assemblies can be modeled for Fig-6-8. Fig 8 has a structure that is yet unknown, the periodic bright circles remain unexplained. Figure 6 has a pattern discussed by Brandow et. al. ⁽²⁰⁾





Diagram4

Diagram 3 Displays the possible structure for an 8CB liquid crystal as shown in figure 5 with 2.5 nm regions of light and dark. Diagram 4 Displays one 8CB molecule

The periodicity of the structure in figure 5 is roughly 5 nm. This is spaced equally into 2.5 nm regions of light and dark. We suggest a possible structure that is shown in Diagram 3. Dipole-dipole interactions would make this head-to-head, tail-to-tail order the most promising theory, explaining both dark and light regions as well as the periodicity. Patterns for Figure 7 and 8 have yet to be determined. Figure 7 most likely has a pattern similar to Figure 5. The periodicity is also roughly 5 nm and the length of each small segment is 3.3 nm, which is also similar to figure 5. Figure 8 has a pattern that is somewhat an enigma. A molecular structure that would compare well with this image has yet to be found; we are unsure what the periodic bright circles are. It is possible that the 8CB molecules form a phase unlike the ones reported. It is also possible that the images are the results of different contrast due to different imaging conditions.

Eicosanol was another surfactant we successfully applied to HOPG. This molecule is a long alkane chain with an OH group at one end. 1 mg of Eicosanol, also called $C_{20}H_{42}O$, was mixed with 1 ml of Dodecane or C12H26. The structure of Eicosanol on the surface of graphite is shown below. (Diagram 5) We obtained this structure by considering the length of eicosanol and the periodicity of the assembled structures. The periodicity was too long to be only one eicosanol molecule long, however too short to be two. We therefore concluded that the eicosanol must be at an angle with respect to the normal of the rows. The exact numbers and angles are discussed in diagram 5. The periodicity of eicosanol is 4.8 nanometers. (Figure 10) We suggest that the OH groups are visible as the dark regions that separate the rows. This is because their tunneling current should be less than the alkane chain. The difference in self-assembly between figures 9 and 10 can be attributed to the multiple ways (directions, orientation and periodicity and so forth) self-assembly can occur. Figure 9 displays a disordered state of self-assembly, where many patterns, periodicities and directions are imaged on the same sheet of graphite. Figure 10 displays a more ordered structure that appeared with time, where all rows are the same in direction and periodicity. Stronger lines of self-assembly seem to override weaker self-assembled structures so that after a few minutes only one pattern is seen.







Diagram 5

Eicosanol Self-assembly. Figure 9 is an image of eicosanol as it self-assembles. The assembly is extremely disordered; rows face different directions and some areas are curvy or just a blur. Figure 10 shows a more orderly self-assembly where the distance between rows is consistent and all rows face the same direction. Diagram 5 illustrates a possible structure of figure 10 rows. Allowances are made for the width of the molecule versus the periodicity of the rows.

Our group was also able to achieve images of SDS on a graphite surface (Figure 10 and 11). These images show that SDS forms long rows with a periodicity of roughly 4 nm. Figure 11 shows two different layers of graphite with two different orientations of

SDS rows. This shows that the orientation from different graphite layers is independent of each other. Figure 10, however, shows that the continuation of a certain orientation is possible through different layers of graphite. One can see that the rows continue exactly where they are interrupted by the change in graphite layer. The periodicity in this case is roughly 4.5 nm. A proposed structure of the self-assembled SDS is shown below. Again, functional groups face each other in a head-to- head, tail-to –tail fashion.









Diagram 7

Diagram 8

SDS molecular structure. The molecular structure of SDS rows as seen on graphite (fig 10 and fig 11) and a single pair of SDS molecules. Functional groups face each other again as in previous molecules

4. Conclusion

Images of 8cb molecules and Sodium Dodecyl Sulfate were imaged on a HOPG surface. These images revealed high amounts of self-assembly, forming long, continuous rows. Our images of 8CB on HOPG graphite reveal new or not previously imaged surface structures. The SDS rows agree with those found in the literature. Either of these highly ordered, self-assembling molecules could potentially be used for self-assembled templates. Throughout all three groups of surfactants on graphite, we have observed a common theme in self-assembly; polar groups have a tendency to group facing each other. We suspect that this tendency is because of hydrophobic/hydrophilic affinity to interact with other molecules that share its phobia or lack thereof. Phobic tails and philic heads cluster with other similar molecules. OH groups also have the capability to hydrogen bond to other OH groups, aiding the self-assembly process by ordering molecules into stable hydrophobic and hydrophilic groups. This may also aid in ordering molecules into a homogeneous pattern.

Our hopes are to further our research by continuing this process on a more controllable surface, like Au(111) under potential control. Other experiments include applying two surfactants at once or applying a surfactant subsequent to another surfactant. Further research needs to be conducted on how surfactants form homogeneous structures across a surface. Images of SDS show that patterns can be, however not always are, carried across a step on the surface. Other images of eicosanol suggest that domains with different directions and patterns can form even on a uniform terrace.

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