Pattern Making in Nickel (II)-Octaethylporphyrin Molecules on HOPG with a Scanning Tunneling Microscope

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Introduction

Lots of work has been done in the past on the manipulation of single atoms, molecules, and rows of molecules on a surface with a scanning tunneling microscope (STM) (Figure 4), but little has been done on large area manipulation of molecules to form patterns. In many of the early studies, scientists focused mainly on how the atom interacted with the surface of the substrate in the manipulation. In this experimental case, however, the concern was how the molecules interacted with the tip. In this experiment, I manipulated the molecules by bringing a tip close enough to the surface in that a boxlike structure was formed in the self-assembled monolayer, leaving the high ordered pyrolytic graphite (HOPG) exposed. If this pattern making process can be even further controlled, it will be extremely useful when it comes to nanotechnology.

Experiment

For my experiments, I used platinum-iridium tips (Figure 2a). These tips were electrochemically ion-etched in an NaCl solution. After etching, a tip should be atomically sharp on the order of a few angstroms. Atomically sharp tips are the best at tunneling the electrons (Figure 2b). (Figure 2c) shows the STM used in this experiment.

When I started the experiment, the bias voltage for the STM was set at -0.7 mV, and it remained the same throughout the experiment. The only parameter that changed was the set point current value. This value was initially set at 0.1 nA. The scan rate was set at 4 mm/s. The height of the tip relative to the surface is controlled by the values of bias voltage and set point current. As the current increases (at fixed bias) the tip approaches the surface exponentially. 

First, I scanned the surface for an area containing a dense monolayer of deposited molecules. Upon finding this area, I scanned the area over and over again in a downward direction within a 60x60 nm grid (Figure 2a). I kept scanning until all drift, which could possibly damage the tip at high magnification, was eliminated. While scanning, I also needed to rotate the image until the rows of molecules appeared vertical and horizontal. This rotation makes it easier to manipulate the boxlike pattern on the surface. Once, it was time to make the box. To do this, I changed the set point current value to 6 nA which brought the tip extremely close to the surface. I then made my scan size 100x100 nm in the center of the 60x60 nm grid. I scanned down only once.

The set point current was then reduced to 0.1 nA, I zoomed back out to a 60x60 nm grid and scanned again. Upon scanning, I saw that molecules had been removed from the surface, and that somewhat of a boxlike structure could be clearly seen in (Figure 4b). To make sure the molecules manipulated did not collect elsewhere on the sample, I zoomed out even further to a 200x200 nm image (Figure 4c).

Results and Conclusion

I was able to achieve my objective on this project; molecules were manipulated on surface in a boxlike pattern. Where did the manipulated molecules go? I think the molecules removed from the surface actually collected on the tip. The only issue that came up was that, yes, I created a boxlike structure, but why do the two images look so different from each other? Are they pictures of the same image? The problem comes into play with the set point current value. Instead of lowering it to 0.1 nA when I zoomed out, I should have lowered it even further to about 0.05 nA. The reasoning behind this is that the molecules that formed the edge of the box were now more weakly bound to the surface than what they used to be. Van der Waals bonds had to be broken in order for the manipulation to have occurred. The manipulated molecules took away some of the bond strength within the remaining ones. This means that as I scanned the bigger picture, the molecules on the perimeter of the boxlike structure, still sensing a strong enough current to move, just manipulated themselves to form a new structure on the surface. This is why (Figures 4d, e) look so different, but they are still the same image, just at different magnifications.

Acknowledgements

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References
(1) http://www.nanoscientists.com/NiOEP/NiOEP.html
(2) http://www.pacificnanotools.com/asma-modules/single.html
(3) http://stereo.ase.edu/nmodules/spmmod/senses.html

Figure 1: IBM’s extensive research with manipulation. Left: IBM written with single atom manipulation (2).

Figure 2a: Platinum iridium tip. (1).

Figure 2b: Diagram of tunneling (4).

Figure 2c: STM used in this experiment.

Figure 3: Chemical structure NiOEP molecule. The following elements are represented: 
Ni is in red
C is in blue
H is in yellow
N is in dark gray
O is in white

Figure 4a: Triclinic NiOEP lattice in a 60x40 nm grid.

Figure 4b: Tetragonal NiOEP lattice in a 60x40 nm grid.

Figure 4c: Tetragonal NiOEP lattice in a 30x20 nm grid.

Figure 4d: Tetragonal HOPG lattice in a 4x3 nm grid.

Figure 4e: Tetragonal HOPG lattice in a 10x6 nm grid.

Figure 5a: 60x60 nm grid before the manipulation.

Figure 5b: 60x60 nm grid after the manipulation.

Figure 5c: 100x100 nm grid after manipulation.

1(Cu)0.75H0.25Ni0.25N

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