USING CURRENT SENSING ATOMIC FORCE MICROSCOPY
TO STUDY HETEROGENEOUS MATERIALS

A THESIS IN
Physics

Presented to the Faculty of
University of Missouri - Kansas City in Partial Fulfillment of
the Requirements for the Degree

MASTER OF SCIENCE

by
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Kansas City, Missouri
2012
USING CURRENT SENSING ATOMIC FORCE MICROSCOPY
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ABSTRACT

Two kinds of heterogeneous materials, block copolymer films and Nafion membranes, are studied by using current sensing atomic force microscopy (CSAFM). In the calculated results, correlation between surface morphology and surface conductance images is obtained using CSAFM, and the implication of the surface conductance and its variations is analyzed. It is found that if the diameter of the CSAFM probe tip is much smaller than the correlation length of the surface morphological features, the current sensing image obtained using the probe has little correlation with the surface morphology, and the current sensed by CSAFM indeed reflects the variation of local resistivity on the sample surface. In experimental results, the microphase separation of block copolymer and the current passing through the ion channel in Nafion membranes are observed by CSAFM. This demonstrates that CSAFM is a powerful and important tool for studying heterogeneous materials.
The faculty listed below, appointed by the Dean of College of Arts and Sciences, have examined the thesis titled “Using Current Sensing Atomic Force Microscopy to Study Heterogeneous Materials” presented by Yucong Liu, candidate for the Master of Science degree, and certify that in their opinion it is worthy of acceptance.

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ACKNOWLEDGEMENTS

First of all, I would like to specially thank my research advisor, Dr. Zhu. His intelligence and enthusiasm had inspired me a lot in the past to overcome all the difficulties encountered during my research and writing papers. His patience and advices really did help me a lot to complete my graduate study.

Second, my special gratitude goes to Dr. Ching and Dr. Wrobel, for being my committee members, reading my thesis and giving me advices. Their supports are really grateful.

Third, I would like to thank all my group members and coworkers, Osung Kwon, Fei Wu, Jiayu He, and Sheng Qin, for their efficient assistance not only in research but also in my everyday life. Also, I want to thank all the faculty and staff members and all my fellow students in Department of Physics. I really enjoy studying and working with them.

Finally, I would like to thank my family and my friends in China for their financial and spiritual support.
To my dear parents and my friend Dayu Wang
CHAPTER 1
INTRODUCTION

1.1 Heterogeneous Material

One of the objectives of material science is to understand the structure/property relations and control microstructures of material which has desired properties based on these relations.\(^1\) Focus of the material science in the past has been on homogeneous materials, such as single crystals, but the field has been growing towards the studies of heterogeneous materials in recent decades, partly due to the rapid development of nanosciences and technologies.

Heterogeneity means lacking uniformity. A heterogeneous material refers to a material which is composed of domains of different components or phases.\(^1\) And the microscopic length of the different domains in heterogeneous materials is usually much larger than the molecular size but much smaller than the macroscopic sample size, which is illustrated in Figure 1.1.\(^1\) In nature, there are many examples for heterogeneous material, such as particulate composites, interpenetrating multiphase composites, colloids, gels, phase separated metallic alloys and block copolymers.\(^1\)

Unlike the uniformity in structure and properties of homogeneous materials, heterogeneous materials usually have microphase separation which gives them versatile properties in nanoscale. In order to understand the microstructure and properties relations of heterogeneous materials, new techniques are needed, such as powerful microscopes, instead of the ordinary experimental methods such as X-ray diffraction, etc.
There are many advantages and applications for heterogeneous material. In the following, we will introduce two examples to illustrate the properties and application of heterogeneous material.

**Figure 1.1.** Random two-phase heterogeneous materials. $L$ represents the macroscopic length and $l$ represents the microscopic length.

1.2 Block Copolymer

Block copolymers are hybrid macromolecules formed by coupling together two or more chemically distinct homopolymers.\[^2\] It can be separated into different domains of polymer components on the nanometer scale due to the different polymer segments’ inherent incompatibility.\[^3\] So block copolymers are typically heterogeneous material.
The copolymer is a “diblock copolymer” if it contains two chemically different homopolymers, and similarly the triblock copolymer has three different blocks, multiblock copolymer has more, etc. The two chemically distinct homopolymers could form different phases in a self-assembling process, and there are two types of polymer chains which are used to construct the diblock copolymer when we consider its microphase separation: coils and rods. A coil is a flexible polymer chain that prefers to adopt an amorphous “random walk” conformation. On the contrary, rod means the polymer chain is rigid, crystalline, unidirectional and high electron mobility, due to its overlapping π-orbitals.[4]

Coil-coil block copolymer has a simple construction and its phase behavior has been studied for several years, so the heterogeneous microphase separation behavior can be explained through this example. The phase diagram of coil-coil block copolymer is illustrated in Figure 1.2. Flory-Huggins parameter or interaction enthalpy ($\chi$) describes the interaction between two polymer segments. The negative value of $\chi$ means the two polymer segments are similar to each other, and positive value means they are different from each other. And the product $\chi N$ ($N$ is the total degree of polymerization of copolymer (entropy factor)) is usually used to describe the segregation of two segments. When $\chi N$ is less than 10, there is a weak segregation and this segregation effect will generate a disordered morphology. In physics, it means the self-assemble effect is not enough to overcome the entropic penalty. And when $\chi N$ increases, microphase separation can be observed and it also depends on another parameter, the relative volume fractions ($f$).[4]
Figure 1.2. Phase diagram for a conformationally symmetric AB-type diblock copolymer predicted from the self-consistent mean-field theory, in which $L$ denotes a lamellar phase, $C$ or HEX donates a hexagonally packed cylindrical phase, $G$ denotes a bicontinuous $la\overline{3}d$ cubic, $S$ denotes bcc spheres, CPS denotes close-packed spheres, and DIS denotes a disordered phase. Dashed lines denote extrapolated phase boundaries, and dot lines denote the mean-field critical point. $\chi$ is the Flory-Huggins parameter or interaction enthalpy, and $N$ is the total degree of the polymerization of copolymer. $f_A$ refers to the relative volume fraction of A component. $^{[5]}$

The different nanostructures adopted by coil-coil block copolymers with different relative volume fractions have been illustrated in Figure 1.2. When $f = 0.15$, the minority polymer segments will form spheres, and the majority block will surround them continuously, which is structure $S$. And if $f$ increases to the range of $0.2 – 0.35$, the hexagonally packed cylinders will be formed by the minority component. This structure is referred as $C$ or HEX. Larger values of $f$ like $0.35 – 0.4$ will make the minority
component create the gyroid (G) structure, but it is still less than the majority component until $f = 0.5$ which will form the lamellae (L) structure.\^[4]\]

One of the applications for block copolymers is to use them as the active layer in organic photovoltaics (OPVs), as the microphase separation of the block copolymer could form donor domain phase and acceptor domain phase, and each kind of domain is connected (only the spherical structure above has isolated domains) and provides continuous path for the traveling of electro-hole pairs to their electrodes. This block copolymer could be considered as the candidate for OPVs application. One example is the block copolymer PS-Mo-PT. The structure has been illustrated in Figure 1.3. Poly(3-hexylthiophene) (PT) acts as the donor and Mo is the acceptor.

![Figure 1.3. The structure of block copolymer PS-Mo-PT.](image)

1.3 Proton Exchange Membrane—Nafion

The proton exchange membrane (PEM) is a crucial component in $H_2/O_2$ fuel cells.\^[5] Nafion, a perfluorosulfonate polymer which was developed by E. I. du Pont de Nemours and Co, is recently the most widely used PEM membrane due to its chemical and thermal
stability, and high, selective permeability to water and small cations, in particular protons.\cite{6}\cite{7} Nafion is constructed by adding hydrophilic ionic side groups to a hydrophobic Teflon-like backbone. The chemical structure is illustrated in Figure 1.4. Obviously, it is a heterogeneous material due to its two chemically different segments.

\[ \text{Figure 1.4. The chemical structure of Nafion.} \]

Equivalent weight (EW) is the number of grams of dry Nafion per mole of sulfonic acid groups when the material is in the acid form.\cite{7} For example, there are around 14 CF\textsubscript{2} units in the side chains of membrane 1100EW. Common writing is Nafion 115 films, 115 referring to a film having 1100 EW and nominal thickness is 0.005 in.\cite{8}

For Nafion membrane, the sulphonated side chains are highly hydrophilic which will create a region with a quantity of water, and dilute acid was created in this region due to the SO\textsuperscript{3−} group’s weekly attraction for protons. This property induced the microphase separation of Nafion membrane, the dilute acid region and hydrophobic region. So understanding the morphology of Nafion membrane is crucial to build the
relations between structure/property and push the performance limit of the Nafion membrane in fuel cells.

The structure of Nafion membranes is complex and intrinsically heterogeneous.\textsuperscript{[9]} Despite decades of research and some successful applications of Nafion, their morphology remains the focus of debate in current literature, such as cluster-network model, modified core-shell, lamellar model, sandwich-like model, and water channel model, etc.\textsuperscript{[9]} By looking at those phenomenological models of Nafion membranes, we can conclude the model of Nafion membranes as the phase separated morphology consisting of discrete hydrophobic and hydrophilic domains. The hydrophobic domains were formed by the polymer fluorocarbon backbones and side chains, and hydrophilic domains are composited by the ionic groups and the water molecules around them as we described before. This model has been illustrated in Figure 1.5. When the water in the hydrophilic domains increases, the size of these domains will also increase and eventually percolate over the membrane to form a random ionic conducting channel network which could provide a continuous pathway for ionic conduction.\textsuperscript{[9]} These results have been observed by using small-angle X-ray scattering and neutron scattering, transmission electron microscopy and scanning probe microscopy.\textsuperscript{[9]}
Figure 1.5. Illustration of hydrophilic and hydrophobic domains in a Nafion membrane. Hydrophilic domains are composited by the sulfonic acid groups (–SO$_3$H) and the water molecules attracted by them (blue colored). The yellow colored part refers to the hydrophobic domain matrices formed by the polymer backbones and side chains.$^{[9]}$

1.4 Experimental Method for Studying Heterogeneous Materials

Recently years, the heterogeneous materials grew more and more importance in industrial applications due to their tailored electronic and other properties tunable at the nanometer scales. This trend makes the characterization of these materials and the evaluation of their performance in nanoscale increasingly important.$^{[10-12]}$ In consideration of characterizing the microstructure and properties of heterogeneous materials, powerful microscope techniques are needed to study and investigate the
morphology and other properties of them. Among the various techniques, the current sensing atomic force microscopy (CSA FM) has become a versatile and powerful tool used in probing the structures and the local charge transport properties of nanostructured materials.\[13-25\]

There are three kinds of microscopes: optical microscope, electron microscope and scanning probe microscope. The optical microscope is the most common type of microscope, containing a series of optical lenses which can produce an enlarged image of sample when light passes through them. The magnification and resolution of optical microscope have limits due to the diffraction of light. The electron microscope was developed from the optical microscope, using electrons rather than light to generate the image, so it has a greater resolving power than the optical microscope. But electron microscopes are expensive to build and maintain, and the samples have to be observed in vacuum, which limits the application of it. The scanning probe microscope is different from the optical and electron microscopes because it forms images of sample surface by using a physical probe scan the surface line by line and record the probe-surface interaction as a function of position. So the resolution of the scanning probe microscope is not limited by diffraction, but only by the size of probe, which gives it much higher resolution. Besides, when the probe is scanned across the sample surface, interactions between the tip and sample are detected and mapped. Different techniques sense different interactions, which can be used to describe surface topography, adhesion, elasticity, electrostatic charge, local conductivity, etc. What’s more, the interactions can be used to modify the structure of sample, which is called the nanolithography. Those advantages
give scanning probe microscope wide application in material science and surface science, especially in characterizing the micromorphology of heterogeneous materials.

The atomic force microscope is a high-resolution scanning probe microscope. It has a cantilever with a sharp tip in the end which is used to scan the sample surface. The cantilever is attached with a (x, y, z) scanner made of piezoelectric materials which could move the probe across the sample and back over each line of the image area. For each (x, y) coordinate pair, the interaction of the tip and sample is recorded as one data point. The collection of data points is then synthesized into the image, a 3-dimensional map of the surface characteristic being examined. The most common AFM image is the topography image, in which the third dimension, z, for any given (x, y) coordinates, is the relative height of the sample surface. When the tip is approaching the sample surface, the interaction force between the tip and surface will induce a deflection of the cantilever which has a correlation with the distance, or relative height. The deflection can be measured by a laser reflected from the end of the cantilever into a photodetector as illustrated in Figure 1.6. Besides, the feedback signal controls the vertical movement of the scanner.
Figure 1.6. The schematic of an atomic force microscope. Accessed from Osung Kwon’s dissertation with permission.

AFM can be operated in different modes: contact mode, non-contact mode and tapping mode. In contact mode, the tip has soft contact with the sample, and the repulsive force becomes the domain interaction and causes the deflection of cantilever. A sensitive electric current measuring loop can be applied in contact mode AFM, which creates the current sensing atomic force microscopy (CSAFM), a novel technique which can measure the morphology and conductivity of the sample surface at the same time. CSAFM is a versatile and powerful tool to study the heterogeneous materials, especially the block copolymer and Nafion membrane which has microphase separation that induced various levels of conductivity. This will be introduced in detail in Chapter 2.
CHAPTER 2
EXPERIMENTAL SET-UP

2.1 Introduction to CSAFM

As discussed in Chapter 1, Current Sensing Atomic Force Microscopy (CSAFM) has obtained great attention as a versatile and powerful tool used in probing the structures and the local charge transport properties of nanostructured materials. This technique offers the unique capability of simultaneously mapping surface morphology and local charge conductance with nanometer or even molecular resolution. The distinctiveness of a CSAFM is its capability to distinguish topological features on a sample surface that are more conductive from those that are less conductive. In addition, CSAFM allows current-voltage (I-V) characteristics to be measured at select points of the current sensing image to gain insight on the mechanisms that govern the local charge transport behaviors of the materials. These features of CSAFM make this technique particularly suitable for studying materials with heterogeneous structures at the nanometer scales, such as nanocomposites, semiconducting copolymer films, and ionic exchange membranes.[13-25]

The configuration of a CSAFM is a conventional atomic force microscope (AFM) with a sensitive electrical current detecting circuit connecting the conductive probe tip in the AFM to a plane electrode placed beneath the sample being scanned.[17-20] The probe tip is usually a conventional AFM tip coated with a metal layer. As a CSAFM is operated under a contact mode with a constant bias voltage applied to the tip, the tip probes the surface morphology and detects the current between the tip and the sample.
simultaneously. The current detected by a CSAFM is related to the electrical resistance between the probe tip and the plane electrode. Since the tip used is usually very sharp, it is generally believed that the current detected is sensitive to the local electrical conductivity (or resistivity) near the region contacted by the tip. Thus the instrument is also termed as a scanning-conductive AFM. If the tip is biased with an alternative voltage, the ac-current detected at different locations is considered to map out the surface impedance on the sample.[15]

The conductance mappings obtained using a CSAFM reveal contrast between good and poor conducting regions on a sample surface. However, in characterizing nanostructured materials for electronics devices and other applications, it is often desirable to have a quantitative assessment of local conductance variation associated with the nanostructures intrinsic to the materials or purposely fabricated in the devices. Owing to the point contact configuration of a CSAFM in measuring the current flown across a sample, obtaining the conductance from the measured current is not straightforward, and several factors which may affect the determination of the conductance need to be considered. In the following we will analyze how the sample thickness, in comparison to the size of a CSAFM probe tip, and sample surface morphology affects the current sensing measurements and thus the determination of the local electrical conductance. We will also show that for a probe with the tip radius much smaller than the sample thickness, the measured current under a constant bias voltage depends on the tip radius only, while for tips with radius larger than the sample thickness, the measured current under a constant bias follows the Ohms resistivity relationship with the tip contact area and the sample thickness. We will further demonstrate that current probed by a CSAFM is
sensitive to the heterogeneity in the surface layer with a thickness comparable to the tip diameter and the resolution of current sensing images are limited by the probe size.

2.2 CSAFM Measured Surface Resistivity

The current sensing system in CSAFM is a two-terminal probe of the electrical transport between a sharp conducting tip and a plane electrode, as illustrated in Figure 2.1. The measured electrical current flows through a channel which consists of the tip and the sample connected in a series: the total resistance of the channel would be the sum of that from the tip, the sample and contact resistance. This tip-sample configuration is similar to that considered in a recent study of contact resistance between dissimilar materials. The contact area between the tip and sample is usually very small, with the radius of the contact typically being on the order of several nanometers to several tens of nanometers, and thus the resistance in the channel is dominated by the contact between the tip and the sample. The electrical contact resistance between two objects of the same material can be described by the so called Holm resistance if the dimension of the contact is much smaller than that of the objects. For dissimilar materials, the contact resistance between them was found to differ from that between the same materials by about 8%. Thus, if the sample thickness $d$ is much larger than that of the tip radius $r$ ($r \ll d$), the contact resistance can be approximately be expressed in terms of Holm’s resistance:

$$R_{\text{H}} = \frac{\rho}{4r},$$

where $\rho$ is the local resistivity on the sample surface. In this case, the measured resistance (the ratio of the bias voltage and the measured current) depends only on the local surface resistivity and the radius of the probe tip. If the contact area between the tip and the
sample surface remains a constant while the tip scans across a sample surface, the current sensing image should reflect the conductance distribution on the surface.

![Diagram](image)

**Figure 2.1.** Illustration of the experimental set-up of the current sensing atomic force microscopy (CSAFM) for the study of heterogeneous materials. The probe tip was coated by metal as the current sensor, and when a voltage is applied between the tip and substrate, the current signal passing through the tip and sample surface will be recorded in the given X/Y coordinates to map a current sensing image for the sample surface.

Another scenario is considered here in which the sample thickness is smaller than the diameter of the probe tip, then the electrical field in the portion of the sample being sandwiched in between the tip and the plane electrode is approximately uniform and the current flow in parallel in the sample between the two electrodes. Thus the resistance measured using a CSAFM depends on the sample thickness following a standard relation

\[ R = \frac{\rho l}{\pi r^2} \]

To evaluate how the measured current depends on the sample thickness and the size of the probe tip, we calculated the resistance between a probe tip with a given radius \( r \) and an electrode attached to the other side of a sample of thickness \( l \), using a finite
element analysis method, in which we consider a disk shaped sample with a conductivity
0.1 S/m and thickness $l$ with one side grounded and the other side contacted by a
cylindrical shaped good conductor probe with radius $r$. Solving the electrodynamics’
poisson's equations in a meshing subdomain setting, we obtain the current flow from the
tip to the ground, and thus obtain the resistance across the sample. In Figure 2.2 we plot
the calculated resistance as a function of inverse radius of the probe tip for samples with
different thickness. The solid line represents Holm resistance. It is clear that for small tip
radius (larger $r^{-1}$) the resistance follows Holm resistance almost exactly (independent of
the sample thickness $l$), while for larger tips (smaller $r^{-1}$), the resistance depends on the
sample thickness. The crossover between the two regimes is at $l/r = \pi/4$, when the
thickness of the sample and the tip radius are comparable. In this case, the measured
resistivity does not only depend on the tip radius, but also on the sample thickness. As
mentioned above, the radius of an AFM tip is typically less than several nanometers.
Thus, only when the thickness of a sample is on the order of nanometer or less, the
surface morphology and the current sensing would not display any correlation.
Figure 2.2. Calculated resistances between a sharp tip and planar as a function of the inverse radius of the tip for samples with different thicknesses. The thicknesses of the films are 1 µm (dot line), 2 µm (dash dot line), 4 µm (dash line), 8 µm (short dash line) and Holm resistance (solid line). The resistivity of the film is 10 Ω·m. Insets are the electric potential contour line (0.1 V for each interval) and the current line (longitudinal direction).

2.3 Effects of Surface Morphology to Current Sensing Images

The surface morphology of a sample may result in the variation of contact area between an AFM tip and the surface and thus the current flows between the two under a constant bias voltage. Such a situation can be illustrated by considering a conducting tip scanning across a rigid stepped surface, as illustrated in Figure 2.3(a). Assuming the local conductivity on the sample surface is uniform, as a CSAFM tip scans cross the steps, the current detected by the CSAFM remains constant except at bottom of the step edge where the side of the tip is in contact with the step, resulting in an increase in the contact area. Consequently, the current sensing image shows a sharp bright strip at the step edge, as
illustrated in the current profile in Figure 2.3(b) and 2.3(c). To further demonstrate this effect, we imaged a silicon grating (TGZ02, Mickromasch)\(^{[29]}\) using a CSAFM. The grating consists of step strips of 1.5 µm in width and 0.1 µm in height. Indeed, the current detected by the CSAFM across the sample remain nearly a constant except at the grid edge where the detected current shows big spikes which is due to the increase of the contact area between the tip and the surface at the edges of the steps, as illustrated in Figure 2.4.
Figure 2.3. Simulated current sensing image for a tip scanned across a stepped surface. The grade scale reflects the contrast of the sensing currents. (a) Surface morphology profile. (b) Simulated surface morphology image of a surface with the profile shown in (a). (c) Simulated current sensing image of the same surface. Note that the current is constant except at the step edges.
Figure 2.4. A morphological image (a) and a current sensing image (b) measured simultaneously on a silicon grating (TGZ02, Mickromasch).
For surfaces with gradual modulation, we model their varying morphology through a sinusoidal function with an amplitude $A$ and a variation wavelength $\lambda$. The surface height $h(x) = A \sin \left( \frac{2\pi x}{\lambda} \right)$, as illustrated in Figure 2.5(a). For the illustration purpose, we considered the contact area to be approximately proportional to the matching between the local curvature of the surface, measured from above, and that of the tip, i.e., $\left| \frac{1}{a} - h''/[1 + h'^2]^{3/2} \right|$, where $h'$ and $h''$ are the first and second order derivatives, respectively, of the surface height correlation. If the variation wave length $\lambda$ on the surface is much larger than the tip radius $r$, the local curvature of the surface is always much smaller than that of the tip, the variation of the contract area between the tip and the surface remains nearly a constant except when the tip reaches the crests of the sinusoidal surface. Thus, the current sensing image should have no obvious correlation with the surface morphology image except in the regions where surface has protruding morphology. However, if the corrugation length is comparable to the tip radius, the contact area between the tip and the surface varies significantly as the tip scans across the surface. We assume that the contact area is inversely proportional to the difference of the curvatures of the tip and the surface, and have calculated the variation of the contact area as a tip scan across sinusoidal surface. The results are illustrated in Figure 2.5(b) and 2.5(c). The contact area reaches maxima as the tip is in the valleys of the sinusoidal surface, and reaches minima as the tip is at the crests of the sinusoidal surface. The current sensing images would show features which have 90° phase shift comparing to the morphological variation on the sample surface.
Figure 2.5. Simulated current sensing image for a tip scanned across a sinusoidal surface. The grade scale reflects the contrast of the sensing current. (a) Surface morphology profile. (b) Simulated surface morphology image of a surface with the profile shown in (a). (c) Simulated current sensing image of the same surface. Note that the current is constant except at the step edges.

2.4 Sensitivity of Current Sensing to the Surface Conductivity Heterogeneity

It is important to verify that when the variation of the contact area between the tip and the sample is negligibly small, the current sensed by a CSAFM indeed reflects the variation of local resistivity on the sample surface. For this purpose, we carried out a finite element calculation of the resistance between a tip in contact with a conductive film which is homogeneous with the exception of a spherical impurity of a radius 1 nm and
with resistivity higher than the rest of the film. We calculated the resistance of the film sandwiched between a tip of radius 5 nm and a plane electrode with the impurity placed in the different location relative to the tip. Figure 2.6 depicts the relative resistance change due to the impurity placed at different positions directly below the tip. The results indicate that a noticeable change in the resistance occurs when the impurity is located at a distance less than the diameter of the tip beneath the surface of the sample. This is because that as the impurity is close to the tip and it would completely block the pathway of the current, strongly affecting the resistance measured. Thus current sensing images reflect mainly conductivity heterogeneity in a layer, with thickness comparable to the tip size, on a sample surface. We further calculated the resistance of the film sandwiched between the tip and a plane electrode with the impurity placed at different location of the surface layer, to test the lateral resolution in current sensing imaging. Figure 2.7 shows that the relative change in resistance across the film increases noticeably as the position of the impurity is within about twice the diameter of the tip, indicating that the lateral resolution of CSAFM in detecting conductance heterogeneity of the surface layer is usually poorer than that of surface morphology. This result can be easily explained because the current flown is not localized as comparing to the surface force which is used in mapping the surface morphology.

In summary, we have analyzed the possible correlation between surface morphology and current sensing images obtained simultaneously using a CSAFM, and the implication of the measured conductance to the charge transport properties of the sample being studied. We found that morphology and local current sensing images usually do not show correlation except in features associated with step edges or sharp extrusions, where the
contact areas can increase or decrease, respectively. If the size of the probe tip is much smaller than the thickness of the sample, the local current probed should reflect the local charge conducting property in a layer with the thickness comparable to the probe diameter on the surface. If the sample thickness is much larger than probe tip size, the current sensing images should reflect surface conductivity distributions on a sample surface. However, if sample thickness is comparable or smaller than the tip size, the measured current would depend on the tip size as well as sample thickness.

**Figure 2.6.** The relative change in resistance due to the impurity placed at different positions directly below the tip. The differences of resistivity ($\delta \rho/\rho$) between the impurity and the film are: 100% (*dash line*), 30% (*dash dot line*), and 10% (*dot line*), respectively.
Figure 2.7. The relative change in resistance due to the impurity placed at different lateral positions across the film. The differences of resistivity ($\delta \rho / \rho$) between the impurity and the film are: 100% (dash line), 30% (dash dot line), and 10% (dot line), respectively.
CHAPTER 3
RESULTS AND DISCUSSION

In this chapter, we presented experimental results of two kinds of heterogeneous materials which are block copolymers and Nafion membranes, the results obtained by CSAFM demonstrated the wide application and powerful ability of CSAFM in studying the nanostructure and properties of heterogeneous materials.

3.1 Block Copolymer

3.1.1 Preparation of Block Copolymer

As we discussed in Chapter 1, regioregular poly (3-hexylthiophenes) (P3HT) is a good candidate for block copolymer used in OPVs device especially considering its good photo chemical stability and high charge carrier mobility (0.01–0.1 cm$^2$V$^{-1}$S$^{-1}$)$^{[30]}$ The structure of P3HT has illustrated in Figure 3.1.

![The chemical structure of P3HT](image)

Figure 3.1. The chemical structure of P3HT.
The end to end arrangement of side chains structure with the \( \pi-\pi \) stacking of the conjugated backbones given the P3HT high charge carrier mobility.\[^{31}\] In experiments we found the number average molecular weight and processing conditions such as solvent used, annealing conditions and film geometry will affect the charge carrier mobility. From the structure/properties relation, low molecular weight films usually have low charge carrier mobility, due to the isolated of each aggregated domains. Conversely, the high molecular weight films have high charge carrier mobility as the domains are connected well through the long chains, which is known as the chain-packing model.\[^{32}\] And the thermal annealing was supposed to increase the charge carrier mobility of low molecular weight films as it could ordering and overlap the neighboring aggregated domains.

PS-N\(_3\) (polystyrene-N\(_3\)) was used as the coil block in our experiment, and its structure has been illustrated in Figure 3.2. Then the two blocks were joined together through click chemistry. Finally, the hexamolybdate (Mo\(_6\)O\(_{19}\)\(^{2-}\)) cluster was carried out in solvent and attached with the diblock copolymer, resulting PS-Mo\(_6\)-PT, which is illustrated in Figure 3.3. The PT block acted as a donor, and PS-Mo\(_6\) played a role of acceptor to replace the common acceptor PCBM which was also mentioned in Chapter 1. In this process, the molecule weight of PT block can be adjusted to created PS-Mo\(_6\)-PT1, PS-Mo\(_6\)-PT2, PS-Mo\(_6\)-PT3, whose molecule weight were listed below in Table 3.1. (Those samples were prepared by Sanjiban Chakraborty in Dr. Peng’s group, Department of Chemistry, University of Missouri - Kansas City.)
Table 3.1. The molecular weight of each sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>m Value</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-Mo6-PT1</td>
<td>25</td>
<td>4000</td>
</tr>
<tr>
<td>PS-Mo6-PT2</td>
<td>37</td>
<td>6200</td>
</tr>
<tr>
<td>PS-Mo6-PT3</td>
<td>84</td>
<td>14000</td>
</tr>
</tbody>
</table>

Figure 3.2. The chemical structure of PS-N₃.

Figure 3.3. The chemical structure of PS-Mo₆-PT.
3.1.2 Morphology of Thin Films

The morphology of PS-PT blocks and their corresponding hybrid PS-Mo-PT blocks thin film were studied by using CSAFM. Three different sizes of PT blocks and two types of solvents (chloroform and toluene) were used in the sample preparation process in order to understand the effect of molecular size and solvents on film’s morphology. The films were spin coated from the solvents onto indium tin oxide (ITO) glass slides and dried under vacuum which is followed by thermal annealing at around 170 °C for 6 h. The ITO glass substrate enables to get the conducting images with the topography.

The 5 µm × 5 µm topography images and current sensing images of three diblock copolymers PS-PT1, PS-PT2 and PS-PT3 spin coated from chloroform and toluene are illustrated from Figure 3.4 to Figure 3.9. The topography images for the six different thin film samples which include three different molecular weight blocks and spin coated from two types of solvents are no significant different. When a voltage was applied between the Pt coating tip and the ITO glass, the current sensing images for those six samples show an apparently different. Which means the conductivity and structure for each diblock copolymer are different, especially for the rod blocks. From the images we can note that the lowest molecular weight diblock copolymer PS-PT1 spin coating from chloroform has the highest conductivity, however, the medium and highest molecular weight diblock copolymers PS-PT2 and PS-PT are almost negligible conductivity. Conversely, when we studied the conductivity of diblock copolymers spin coating from toluene, the current sensing images show an opposite trend with the molecular weight increased. This means the highest molecular weight PS-PT1 block has the lowest conductivity, while the medium and lowest molecular weight PS-PT2 and PS-PT3 have
high conductive area. From the chain-packing model explained before, the larger molecular weight diblock copolymer should have higher conductivity due to its highly interconnection between each aggregated domain. These contrasting behaviors for the polymers spin coating from chloroform can be explained by the different evaporation rate of solvents. During the dry process, the chloroform has a higher evaporation rate due to its low boiling point (61.2 °C), the higher molecular weight blocks unable to completely self-assembled to well-ordered arrangement in the limit time. But the lower molecular weight blocks take less time to finish the self-assembly, so they exhibited higher conductivity than PS-PT1 spin coating from chloroform. On the contrary, the toluene has a high boiling point (110.6 °C) which will give the high molecular weight blocks enough time to rearrange itself into ordered structure. When both high molecular weight blocks and low molecular weight blocks could completely self-assembled, the conductivity will be determined by the molecular size according to the chain-packing model.[32]
Figure 3.4. CSAFM images of PS-PT1 block copolymer film spin-coated from chloroform on ITO glass. (a) Topographical image. (b) Current sensing image.
Figure 3.5. CSAFM images of PS-PT2 block copolymer film spin-coated from chloroform on ITO glass. (a) Topographical image. (b) Current sensing image.
Figure 3.6. CSAFM images of PS-PT3 block copolymer film spin-coated from chloroform on ITO glass. (a) Topographical image. (b) Current sensing image.
Figure 3.7. CSAFM images of PS-PT1 block copolymer film spin-coated from toluene on ITO glass. (a) Topographical image. (b) Current sensing image.
Figure 3.8. CSAFM images of PS-PT2 block copolymer film spin-coated from toluene on ITO glass. (a) Topographical image. (b) Current sensing image.
Figure 3.9. CSAFM images of PS-PT3 block copolymer film spin-coated from toluene on ITO glass. (a) Topographical image. (b) Current sensing image.
Similarly, the three different molecular size hybrid diblock copolymers PS-Mo-PT1, PS-Mo-PT2 and PS-Mo-PT3 spin coating from chloroform and toluene solvents were studied by using CSAFM. The six diblock copolymers were coated on ITO glasses, and then annealed at 120 °C for 6 h. Due to the hybrid diblock copolymers start degrading around 150 °C, the lower annealing temperature was used here. The 5 µm × 5 µm topography images and current sensing images before and after annealing for each sample have been illustrated from Figure 3.10 to Figure 3.21.
Figure 3.10. CSAFM images of hybrid diblock PS-Mo-PT1 film spin-coated from chloroform on ITO glass. (a) Topographical image. (b) Current sensing image.
Figure 3.11. CSAFM images of annealed hybrid diblock PS-Mo-PT1 film spin-coated from chloroform on ITO glass. (a) Topographical image. (b) Current sensing image.
Figure 3.12. CSAFM images of hybrid diblock PS-Mo-PT2 film spin-coated from chloroform on ITO glass. (a) Topographical image. (b) Current sensing image.
Figure 3.13. CSAFM images of annealed hybrid diblock PS-Mo-PT2 film spin-coated from chloroform on ITO glass. (a) Topographical image. (b) Current sensing image.
Figure 3.14. CSAFM images of hybrid diblock PS-Mo-PT3 film spin-coated from chloroform on ITO glass. (a) Topographical image. (b) Current sensing image.
Figure 3.15. CSAFM images of annealed hybrid diblock PS-Mo-PT3 film spin-coated from chloroform on ITO glass. (a) Topographical image. (b) Current sensing image.
Figure 3.16. CSAFM images of hybrid diblock PS-Mo-PT1 film spin-coated from toluene on ITO glass. (a) Topographical image. (b) Current sensing image.
Figure 3.17. CSAFM images of annealed hybrid diblock PS-Mo-PT1 film spin-coated from toluene on ITO glass. (a) Topographical image. (b) Current sensing image.
Figure 3.18. CSAFM images of hybrid diblock PS-Mo-PT2 film spin-coated from toluene on ITO glass. (a) Topographical image, (b) Current sensing image.
Figure 3.19. CSAFM images of annealed hybrid diblock PS-Mo-PT2 film spin-coated from toluene on ITO glass. (a) Topographical image. (b) Current sensing image.
Figure 3.20. CSAFM images of hybrid diblock PS-Mo-PT3 film spin-coated from toluene on ITO glass. (a) Topographical image. (b) Current sensing image.
Figure 3.21. CSAFM images of annealed hybrid diblock PS-Mo-PT3 film spin-coated from toluene on ITO glass. (a) Topographical image. (b) Current sensing image.
Figure 3.22. 1 µm × 1 µm wide current range CSAFM images of annealed hybrid diblock PS-Mo-PT2 film spin-coated from chloroform on ITO glass. (a) Topographical image. (b) Current sensing image.
Figure 3.23. 0.5 µm × 0.5 µm wide current range CSAFM images of annealed hybrid diblock PS-Mo-PT2 film spin-coated from chloroform on ITO glass. (a) Topographical image. (b) Current sensing image.
From the results, a small different in topography images can be observed after annealing. The structure of films trend to be more ordered after annealing because the material progresses towards its equilibrium state. The current sensing images provided another evidence for the effect of annealing which could be observed from the greatly increased of conductivity for each sample after annealing, especially for the high molecular weight block PS-Mo-PT3 spin coating from chloroform, almost the entire film is covered by conductive regions as illustrated in Figure 3.15. This phenomenon also demonstrated the chain-packing model and the speculation that the high molecular size blocks do not have sufficient time to self-assemble in chloroform solvent. After annealing and completely reorganized, the highest molecular size block PS-Mo-PT3 became the highest conductivity film. For the films spin coating from toluene solvents, the current sensing images illustrated from Figure 3.16 to Figure 3.21 show that the conductivity increase is not so significant compared with the chloroform films after annealing, which is easy to understand for the films spin from toluene have already organized them to quite ordered structure.

Since the current in the high conductive area is already over the maximum measured value especially in annealed samples, the inner resistance in the CSAFM system was replaced by a ten times larger one, so the measured current range was broadened to 100 nA. At the same time, the scan area was concentrated in 1 µm × 1 µm or smaller in order to find more information about the high conductive domains. The new results about sample PS-Mo-PT2 annealed were illustrated in Figure 3.22 and Figure 3.23. The two current sensing images not only illustrated the gradual change of the conductive in those
domains, but also exhibited the high conductive domains mostly located in the boundaries of grains when compared with the topography.

3.1.3 Conclusion

The morphology and conductivity distribution of diblock copolymer films with different molecular size and prepared process were studied by using CSAFM. From the difference in the current sensing images for each film, the block molecular size, the solvents used in spin coating, and the thermal annealing were found to be important to determine the structure of this kind of diblock copolymer PS-Mo-PT. Larger molecular weight blocks show a higher conductivity, this can be explained by chain-packing model. And the conversely results for two solvents may due to the different evaporation rates. Thermal annealing will provide energy for the blocks to break bonds and progresses towards its equilibrium state, so it will increase the conductivity of films.

3.2 Nafion

3.2.1 Membrane Setup

In our experiment, Nafion 115 was used to prepare the fuel cell. At first, the Nafion membrane samples were hot-pressed onto a graphite cathode which was covered with the Nafion solution mixed with the catalyst Pt. Second step, we fixed the home made fuel cell on the sample stage. This step was made by sticking the graphite cathode to the sample stage with carbon paint, in order to build the connection between the cell and instrument. Then the stage was mounted to the CSAFM and a bias voltage was applied the tip and sample stage.
3.2.2 Experimental Results

The experimental results about Nafion 115 samples obtained by CSAFM are listed below from Figure 3.22 to Figure 3.29. The topography image and current sensing image were measured at different bias voltages, and each image has an area of 5 µm × 5 µm.
Figure 3.24. Results of Nafion 115 membrane in 0.8 V sample bias voltage. (a) Topographical image. (b) Current sensing image. (c) The current distribution of current sensing image.
Figure 3.25. Results of Nafion 115 membrane in 0.9 V sample bias voltage. (a) Topographical image. (b) Current sensing image. (c) The current distribution of current sensing image.
Figure 3.26. Results of Nafion 115 membrane in 1.0 V sample bias voltage. (a) Topographical image. (b) Current sensing image. (c) The current distribution of current sensing image.
Figure 3.27. Results of Nafion 115 membrane in 1.2 V sample bias voltage. (a) Topographical image. (b) Current sensing image. (c) The current distribution of current sensing image.
Figure 3.28. Results of Nafion 115 membrane in 1.3 V sample bias voltage. (a) Topographical image. (b) Current sensing image. (c) The current distribution of current sensing image.
Figure 3.29. Results of Nafion 115 membrane in 1.4 V sample bias voltage. (a) Topographical image. (b) Current sensing image. (c) The current distribution of current sensing image.
From the topography images above, the surface of Nafion is uneven and rough which may cause by the bending in the preparation procedure. There is no different for topography images of Nafion in each bias voltage and we can hardly figure out the hydrophobic and hydrophilic domains separation in the model of Nafion membranes in Chapter 1, this is due to the contact area between the tip and the membrane is much larger than the size of the ionic cluster. But we can find the heterogeneous structure due to the hydrophobic and hydrophilic phase separation from the current sensing images above.

The current sensing images are illustrated from Figure 3.22(b) to Figure 3.28(b) from which we can find different conductivity area of the surface. Based on the model of
Nafion in Chapter 1, the high conductive area is composed by hydrophilic domains and those domains are connecting to the channel network as illustrated in Figure 3.29. Conversely, low conductive area is composed by the hydrophobic matrix or disconnected hydrophilic domains on the surface of Nafion.

Figure 3.31. Illustration of the experimental set-up of the current sensing atomic force microscopy (CSAFM) for the study of Nafion. The tip was coated by Pt catalyst. The blue channels present the ionic clusters and water channels, if and only the ionic clusters connected with the channel network could provide a current path for protons.\textsuperscript{[33]}

In order to analysis the conductivity for samples in different bias voltage, the current distribution for each current sensing image was made and illustrated from Figure 3.22(c) to Figure 3.28(c). The peak values for the Gaussian like distributions have been shown in Table 3.2.
Table 3.2. The peak values of current in different bias voltages.

<table>
<thead>
<tr>
<th>Bias Voltage (V)</th>
<th>Peak Value $C_{\text{peak}}$ (nA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>$2.03533 \times 10^{-2}$</td>
</tr>
<tr>
<td>0.9</td>
<td>$4.22803 \times 10^{-2}$</td>
</tr>
<tr>
<td>1.0</td>
<td>$5.38552 \times 10^{-2}$</td>
</tr>
<tr>
<td>1.2</td>
<td>$3.39366 \times 10^{-1}$</td>
</tr>
<tr>
<td>1.3</td>
<td>$8.25904 \times 10^{-1}$</td>
</tr>
<tr>
<td>1.4</td>
<td>3.30217</td>
</tr>
<tr>
<td>1.5</td>
<td>5.72837</td>
</tr>
</tbody>
</table>

The I-V curves for $C_{\text{peak}}$ changing with the bias voltage have been drawn and illustrated in Figure 3.30. From this curve, we can find the significant increase of current occurred when bias voltage is about 1.3 V, this value is very close to the electrolysis voltage of water which is 1.23 V in weak acid solution. Because the tip was coated by Pt which could act as the catalyst in the electrolysis of water, the water in the dilute acid region created by $\text{SO}_3^{2-}$ groups were decomposed to $\text{H}^+$ and $\text{OH}^-$ when the voltage increased to 1.3 V. The created protons passed through the ion channel and reached the cathode which induced more than thousand times increase of the current at a single channel.
3.3 Conclusion

The CSAFM results of block copolymer and Nafion membrane illustrated above provided a large amount of information about the nanostructures and conductivities of these two kinds of heterogeneous materials. For block copolymer PS-Mo6-PT film, current sensing image exhibited the microphase separation clearly. And from studying the current sensing image for each sample, we found the relationship between the nanostructure of film and the conductivity properties. For example, molecular weight will affect the conductive area; films after thermal annealed trended to be ordered which have high conductivities. In experimental results of Nafion membrane, the I-V curve shows the increase of current occurred when the bias voltage increased to the electrolysis voltage of water. This demonstrated the existence of water and they have contribution to the
conductivity of film. These experimental results prove that the CSAFM is indeed a useful tool to investigate the structure/property relation of heterogeneous materials, as it not only can be used to map the 3-D topography image of sample surface but also can be employed to characterize other properties of surface due to microphase/structure separation, like local conductance, adhesion and elasticity etc.
REFERENCES


32. Sanjiban Chakraborty, Synthesis, Morphologies and applications of polyoxometalate-containing diblock copolymers.

VITA

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