Final Project Report for Award DESC0008151

"Trimodal Tapping Mode Atomic Force Microscopy: Simultaneous 4D Mapping of Conservative and Dissipative Probe-Sample Interactions of Energy-Relevant Materials"

Reporting Period: 07/01/2012 – 04/30/2015

Submitted: September 18th, 2015

I. GENERAL AWARD INFORMATION

1. **Award number:** DESC0008151
   Recipient institution: University of Maryland, College Park

2. **Project title:** *"Trimodal Tapping Mode Atomic Force Microscopy: Simultaneous 4D Mapping of Conservative and Dissipative Probe-Sample Interactions of Energy-Relevant Materials"*
   Principal investigator: Santiago D. Solares

3. **Report date:** September 18th, 2015
   Period covered by the report: July 1st, 2012 through April 30th, 2015

II. RESEARCH ACTIVITIES AND OUTPUT

4. Summary of accomplishments:

The key accomplishments for the project were as follows:

a. *Development and commissioning of trimodal tapping-mode atomic force microscopy for simultaneous topographical measurement, compositional mapping and sampling depth modulation*

A new trimodal AFM method was developed initially through computational simulation and then implemented experimentally. The objective was to develop a tool with which users could image buried (subsurface) features under a surface, regulating the level of indentation *in real time and at will*, while providing very high material contrast, simultaneously with the acquisition of the topography. Prior to this development there was no *single-pass* method having all these capabilities. The only alternative were time-consuming volume scans, which also have the disadvantage of not providing feedback on sample damage and morphology in real time. Instead, the results need to be analyzed after the acquisition of the data, without the option to assess whether sample damage is occurring. Figure 1 provides a diagram of the trimodal AFM instrumentation used, which is now available in the PI's laboratory. Figure 2 offers a conceptual drawing of the polymer film/nanoparticle sample used for experimental validation, and Figure 3 provides the experimental results recently published in ACS Nano (the citation is provided in the next section) for a polydimethilsiloxane film with embedded glass nanoparticles.

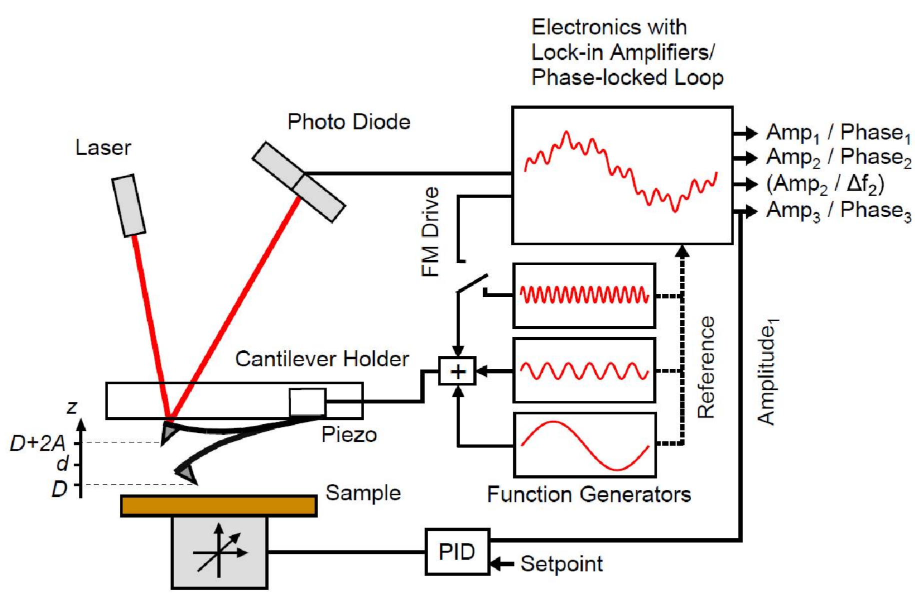

Figure 1. Instrumentation diagram of the trimodal AFM system.

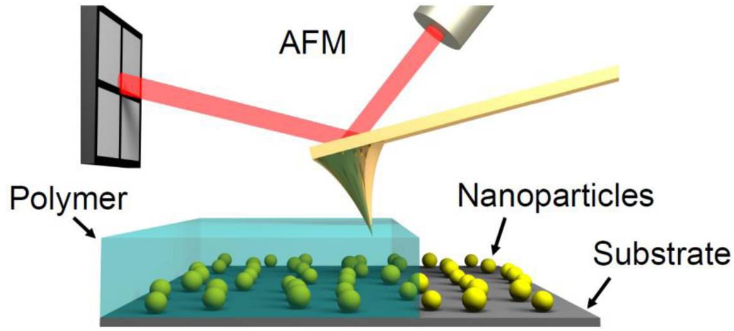

Figure 2. Schematic of a polydimethilsiloxane (PDMS) film deposited onto a silicon substrated coated with glass nanoparticles. The portion of the substrate not coated with the film served as a height reference during the imaging measurements, whereby the polymer surface was scanned while reversibly and gradually controlling the indentation in order to reveal the nanoparticles. The images are provided in Figure 3.

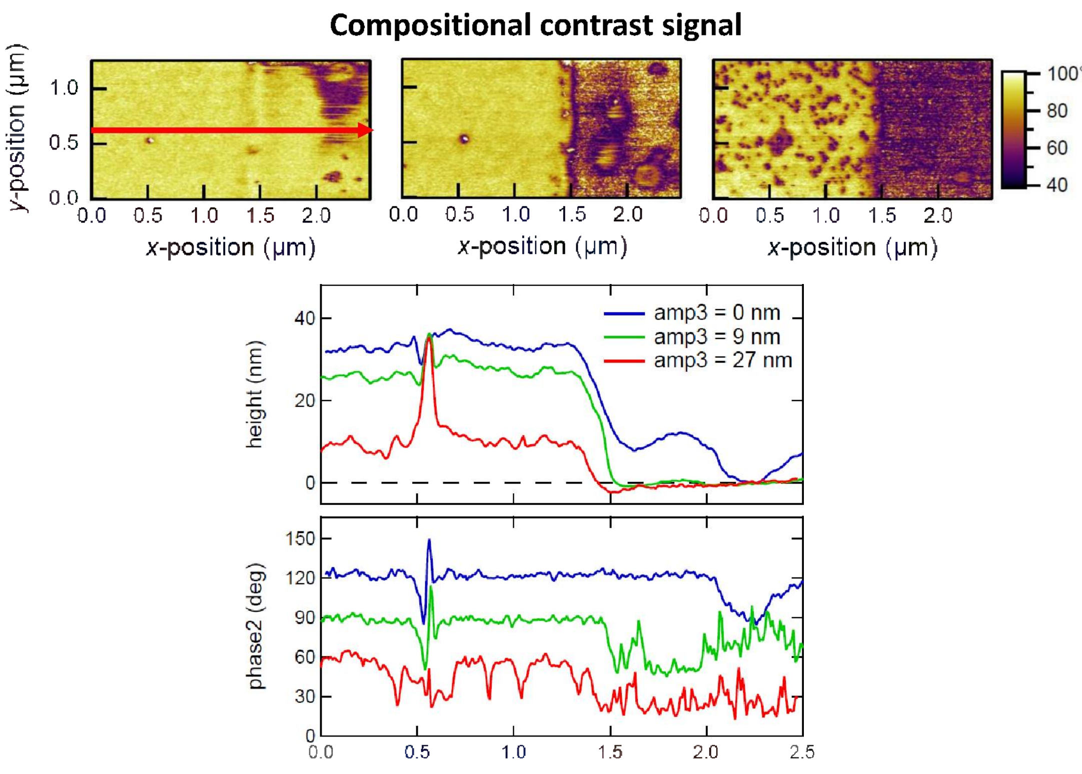

Figure 3. (top) From left to right: compositional contrast images obtained for increasing levels of indentation of the sample illustrated in Figure 2. The nanoparticles and hard substrate are gradually revealed as the indentation level increases. The depth of sampling is regulated in real time by controlling the drive amplitude of the third eigenmode of the cantilever, while compositional mapping is carried out with the second eigenmode. Topographical acquisition is performed with the fundamental mode.

b. Nanomechanical studies of fuel cell membranes

Previous researchers have published AFM images of proton exchange membranes, but none of these studies has examined whether the contrast provided corresponds to the true topography and mechanical behavior of the membranes. All published work relies on single-mode AFM data which does not offer the flexibility to optimize the topographical acquisition and compositional mapping while controlling the level of sample compression. To address this opportunity, nanomechanical mapping was carried out using multifrequency AFM, which as described in the previous sub-section, enables studies with controllable sample compression. Figure 4 shows an example of a feature imaged with single- and dual-mode AFM, illustrating the changes that occur as a result of varying indentation, and Figure 5 shows the corresponding scan lines along the dashed line indicated in Figure 4a. Extensive experiments and numerical simulations were carried out regarding the tradeoffs in sensitivity, sampling depth and topographical measurement accuracy for this type of energy materials and for soft viscoelastic surfaces in general. The results have been published in the Beilstein Journal of Nanotechnology (see publication (e) in the next section).

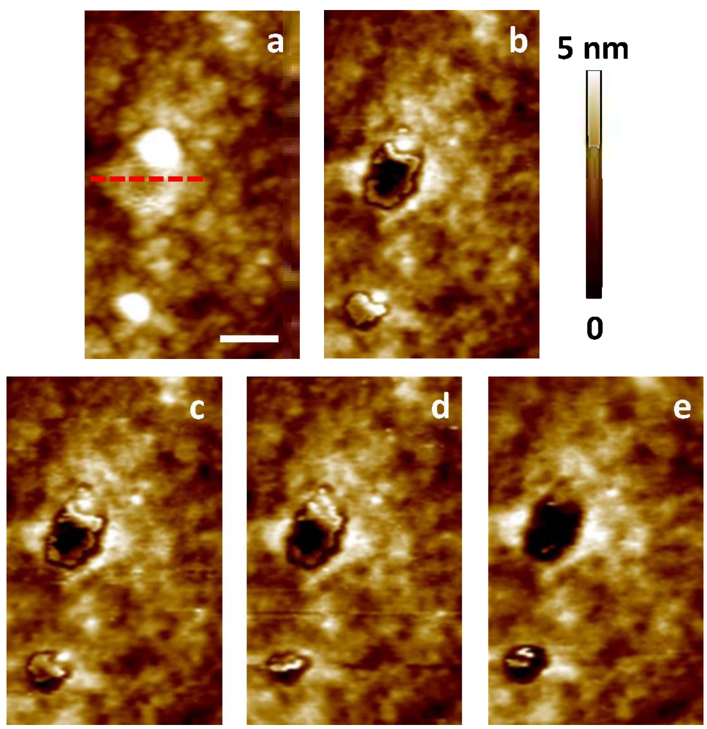

Figure 4. Topographical variation for different imaging conditions for a Nafion® proton exchange membrane. (a) image taken in the attractive (noncontact) regime with single-mode AFM; (b) image taken in the repulsive regime with single-mode AFM; (c) – (e) Images taken with bimodal AFM with increasing level of indentation (see Figure 5 for the scan profiles). The scale bar is 50 nm.

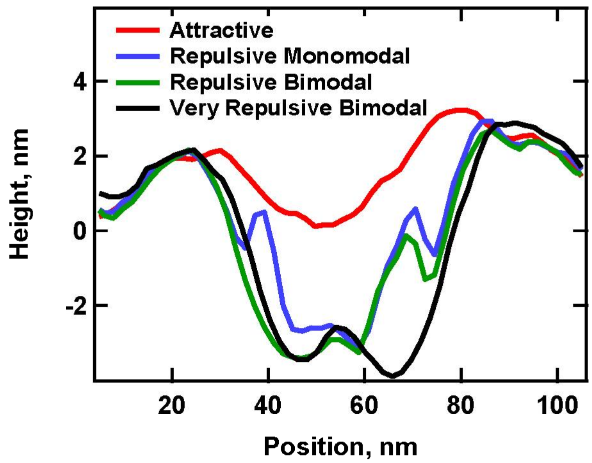

Figure 5. Scan line profiles along the dashed line indicated in Figure 4a for the images shown in Figures 4a (Attractive), 4b (Repulsive Monomodal), 4c (Repulsive Bimodal) and 4e (Very Repulsive Bimodal). There is a clear change in indentation as the imaging conditions become more repulsive. This is an expected result, but one which had not been previously quantified.

c. *Cantilever dynamics studies for multifrequency atomic force microscopy in liquid environments*

Various energy systems of interest involve liquid environments. While AFM can also operate in these environments, the dynamics of the probe are significantly different than those in air such that the assumptions generally made in converting the signals into sample properties are no longer correct. For this reason, a study was carried out to analyze the dynamic complexities encountered as well as their impact on the observables in order to provide users guidelines to evaluate the validity of their interpretations, especially within the context of multifrequency AFM. The focus is primarily on (i) the amplitude and phase relaxation of driven higher eigenmodes between successive tip-sample impacts, (ii) the momentary excitation of non-driven higher eigenmodes and (iii) base excitation artifacts. The results and discussion are mostly applicable to the cases where higher eigenmodes are driven in open loop and frequency modulation within bimodal schemes, but some concepts are also applicable to other types of multifrequency operations and to single-eigenmode amplitude and frequency modulation methods. Figure 6 provides an example of the artifacts observed in single-mode operation, which have been previously studied by others for the standard single-mode tapping-mode case. The current work extends the analysis to multifrequency and frequency-modulation cases, which have become popular in recent years. This work was recently published (see citation (d) in the next section).

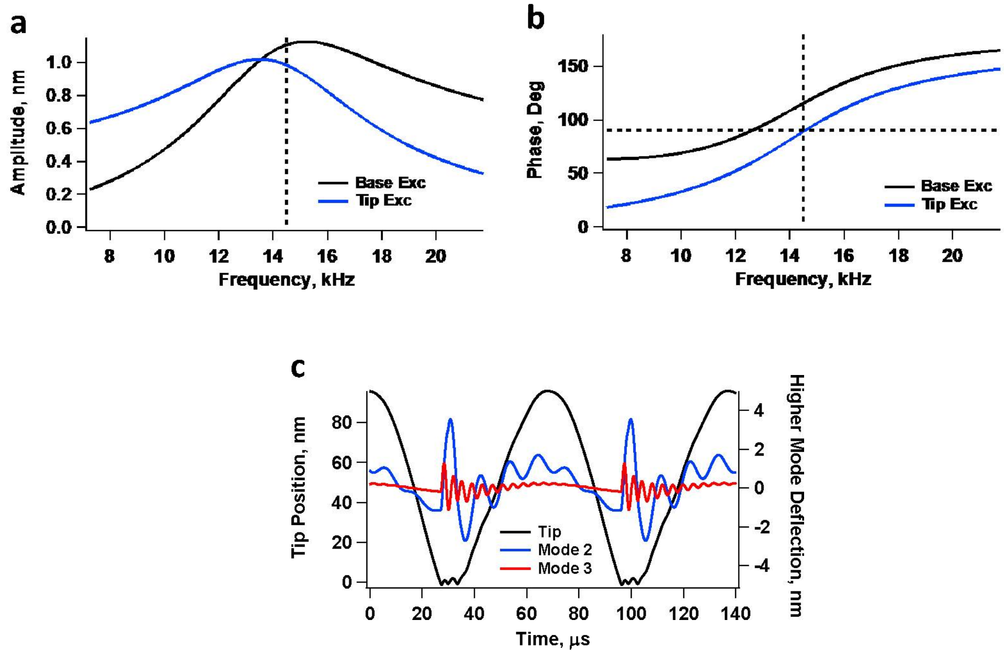

Figure 6. Example of measurement artifacts previously observed in single-mode AFM operation in liquids: distortion of the frequency response (a) and phase response (b) curves with base excitation (the "Tip Exc" traces provide the true response); momentary excitation of higher eigenmodes and multiple tip-sample impacts for every cycle of the fundamental eigenmode (c). The corresponding results for multifrequency methods are conceptually similar although significantly more complex (not shown).

d. *Implementation of atomic-resolution multi-frequency AFM for mineral surfaces immersed in liquids*

Progress has also been made in further developing the experimental capabilities of multifrequency AFM methods for liquid environment studies. In particular, a study was carried out to understand the dynamical conditions under which atomic resolution imaging is possible. While other researchers have successfully imaged atoms in liquids, all previous initiatives have required very sophisticated equipment which was either wholly or in part developed in-house (this is costly and technically challenging), and are limited to single-eigenmode (not multifrequency) imaging. Instead, the current project has focused on the dynamics of the method, such that the desired measurements can be carried out using commercial instruments. Figure 7 shows an example of the type of raw data obtained for different characterization channels (height, first eigenmode phase, second eigenmode phase) for different sets of conditions. For all cases, the observed image corrugation was quantified and directly related to the dynamics of the microcantilever. This work was recently published (see citation (a) in the next section).

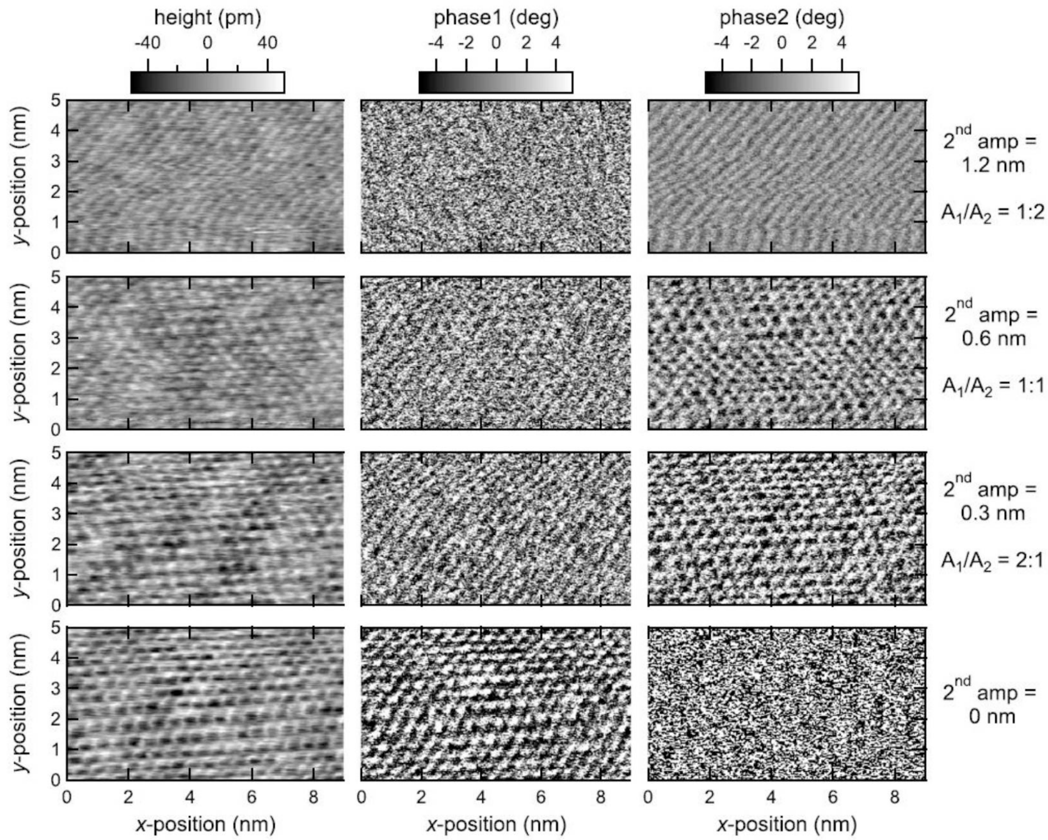

Figure 7. Example of atomic-resolution (raw) images for mica surfaces immersed in water for different characterization channels and imaging conditions.

5. Publications in which DOE is acknowledged:

The journal papers corresponding to this project are as follows:

a) Ebeling, D.; Solares, S.D.; *"Amplitude modulation dynamic force microscopy imaging in liquids with atomic resolution: comparison of phase contrasts in single and dual mode operation," Nanotechnology* **2013,** *24,* 135702 (6 pp).

Acknowledgement text: The authors gratefully acknowledge support from the US National Science Foundation (NSF) and the Department of Energy, through awards CMMI-0841840 and DESC 0008115, respectively.
Note: The DOE funds supported the *experimental* multifrequency AFM dynamics study.

b) Ebeling, D.; Solares, S.D.; *"Bimodal atomic force microscopy driving the higher eigenmode in frequency-modulation mode: Implementation, advantages, disadvantages and comparison to the open-loop case," Beilstein J. Nanotech.* **2013,** *4,* 198-207 (Thematic Series *"Advanced atomic force microscopy techniques"*).

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Note: The DOE funds supported the *experimental* multifrequency AFM dynamics study.

c) Ebeling, D.; Eslami, B.; Solares, S.D.; *"Visualizing the subsurface of soft matter: simultaneous topographical imaging, depth modulation, and compositional mapping with triple frequency atomic force microscopy," ACS Nano* **2013,** *7,* 10387-10396.

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Note: This paper was selected as the feature article of the November 2013 issue and an interview with two of the authors is available as an online podcast (Episode Nov. 2013: http://pubs.acs.org/page/ancac3/audio/index.html#episodes). DOE is acknowledged during the interview.

d) Solares, S.D.; *"Challenges and complexities of multifrequency atomic force microscopy in liquid environments," Beilstein J. Nanotech.* **2014,** *5,* 298-307.

Acknowledgement text: The author gratefully acknowledges support from the U.S. Department of Energy, through award DESC0008115.

e) Eslami, B.; Ebeling, D.; Solares, S.D.; *"Trade-offs in sensitivity and sampling depth in bimodal atomic force microscopy and comparison to the trimodal case," Beilstein J. Nanotech.,* **2014,** *5,* 1144-1151.

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