
# Identification and Validation of Analytical Chemistry Methods for Detecting Composite Surface Contamination and Moisture

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# Introduction

- **Motivation and Key Issues**
  - **Adhesive bonding is now used in manufacture and repair is beginning to predominate over mechanical fastening.**
  - **Adherend surface preparation is a critical issue to the structural integrity and durability of bonded structures.**
- **Objectives**
  - **benchmark knowledge of surface preparation quality assurance methods**
  - **identify and validate definitive analytical chemistry methods to provide sufficient in-field quality assurance.**
- **Approach**
  - **Literature review and analysis (complete)**
  - **Surface chemistry analysis**
  - **Electrochemical sensor study**
  - **Experimental validation**

# Tasks Overview

- Accomplished projects:
  - Electrochemical Sensor Study
  - Humidity Sensor Study
  - Atomic Force Microscopy Study (AFM)
- Current tasks:
  - Advancement of Electrochemical Sensor
  - Chemical Force Microscopy
  - Correlation with other methods

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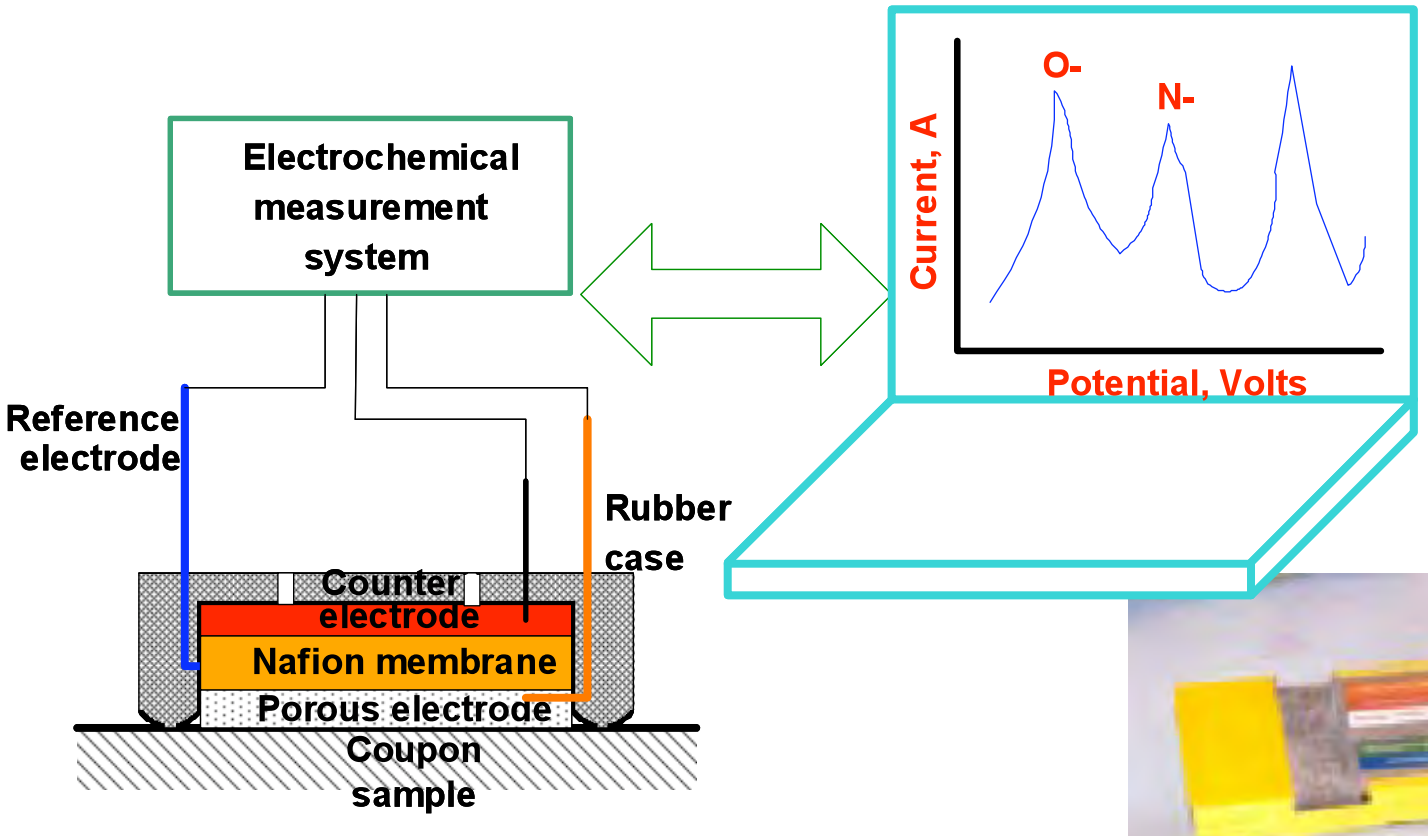
# Solid-State Electrochemical Sensor

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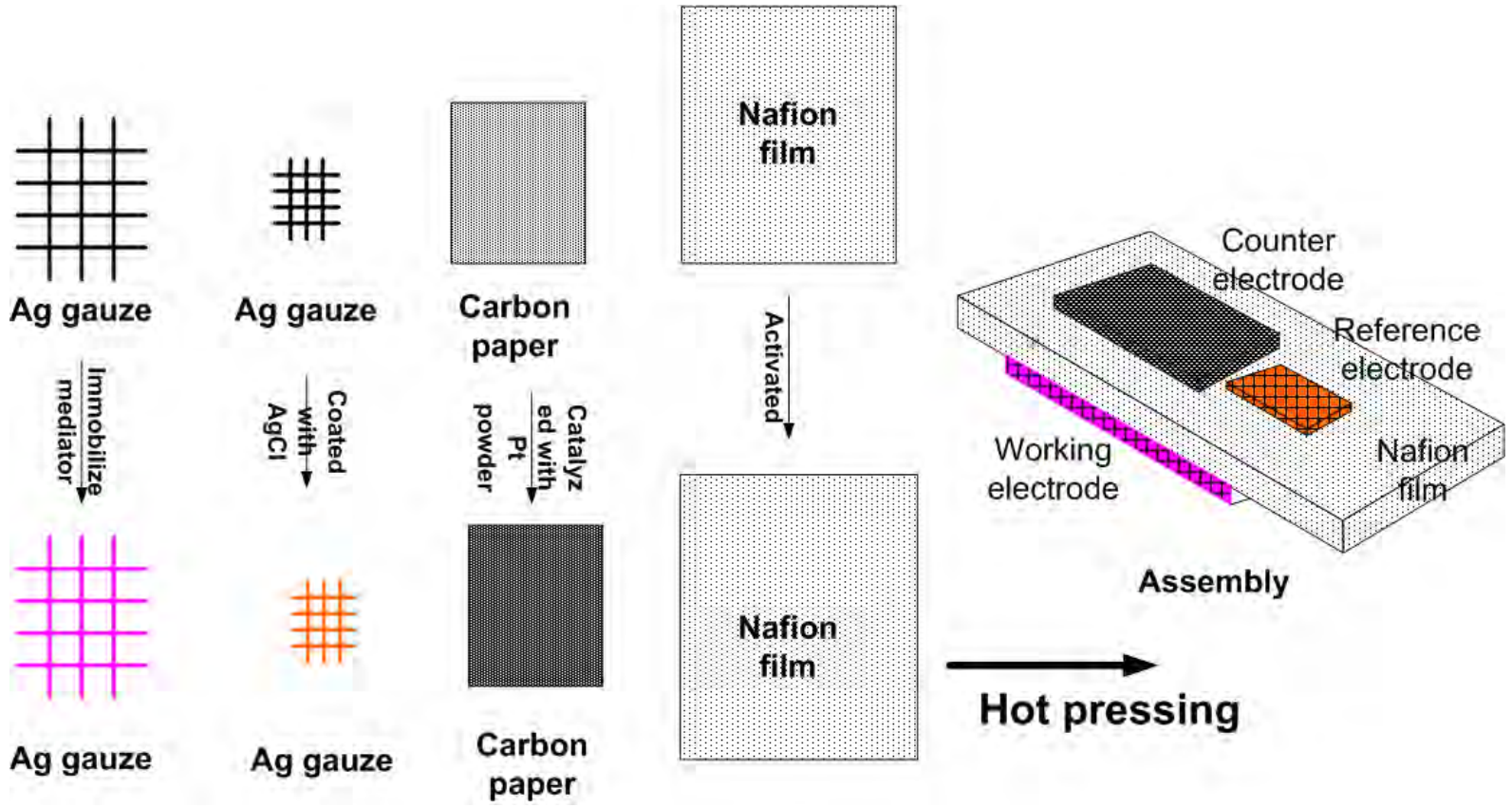
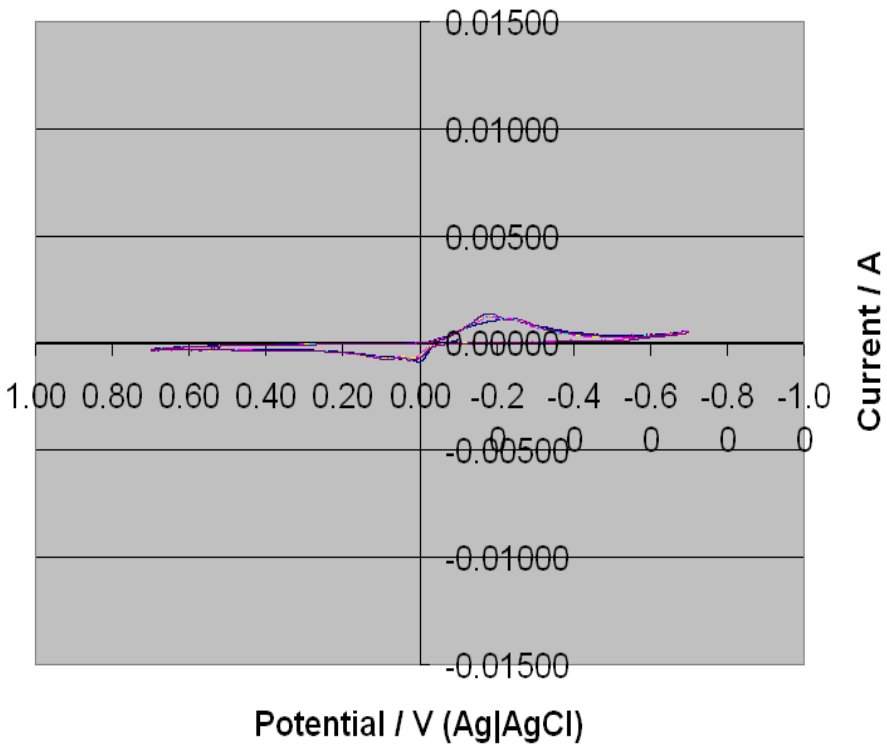
# Fabrication

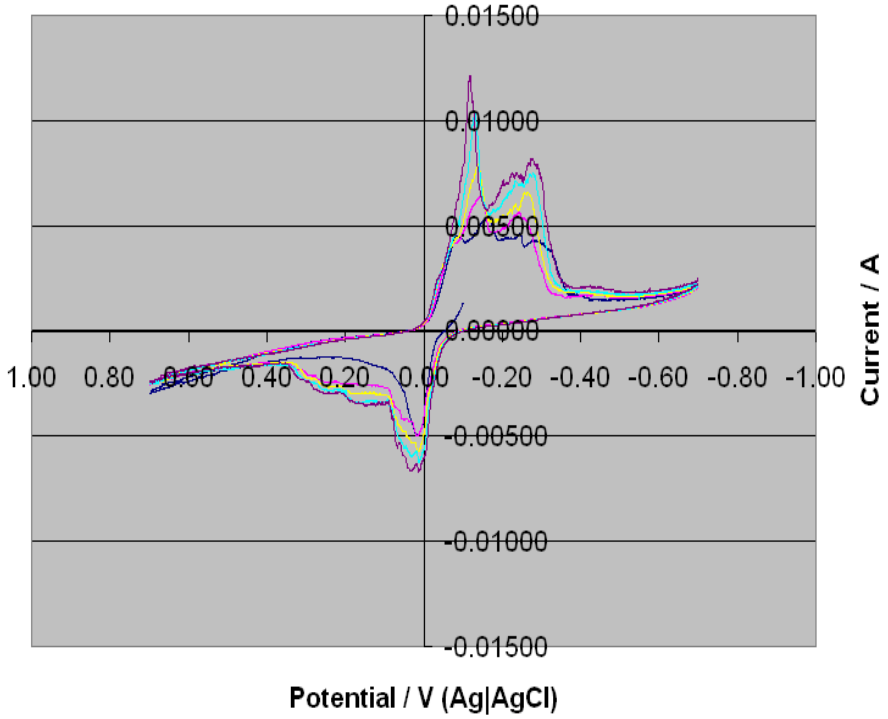


# 2007 Test Results

## Original peel ply sample




## Sulfuric acid treated sample



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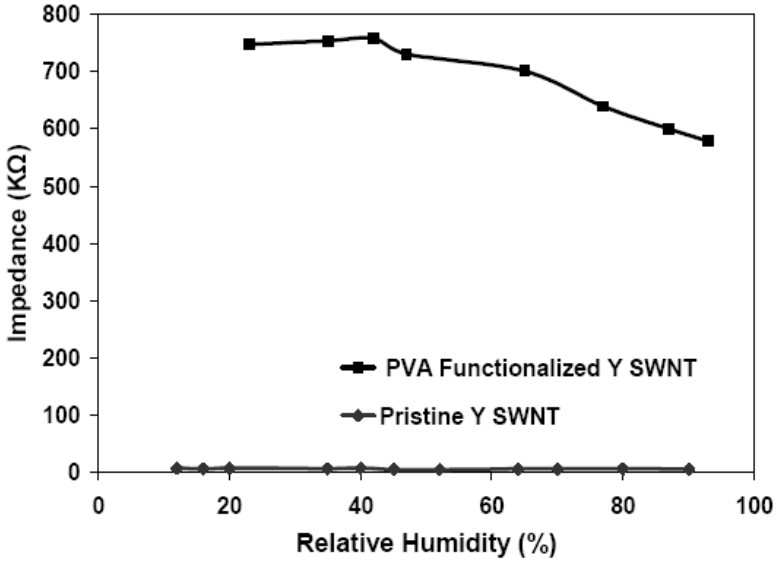
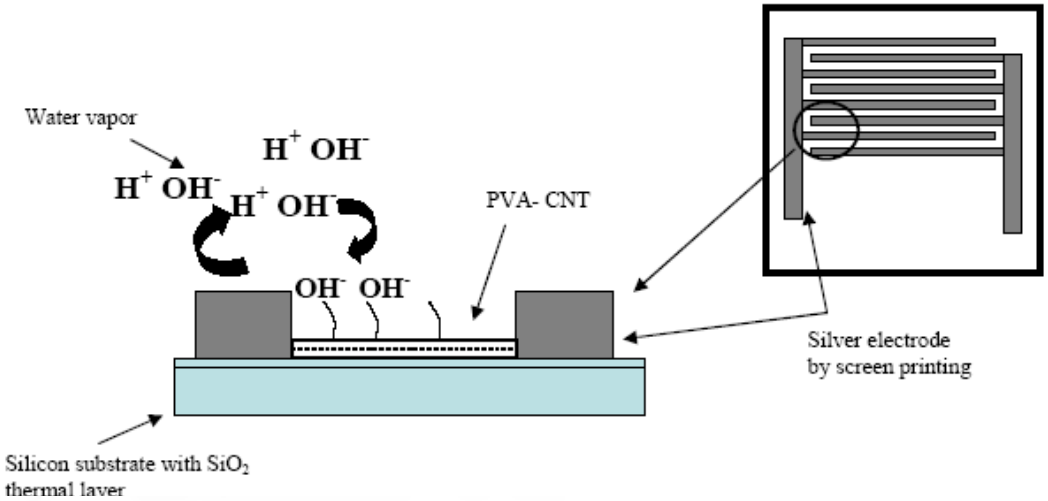
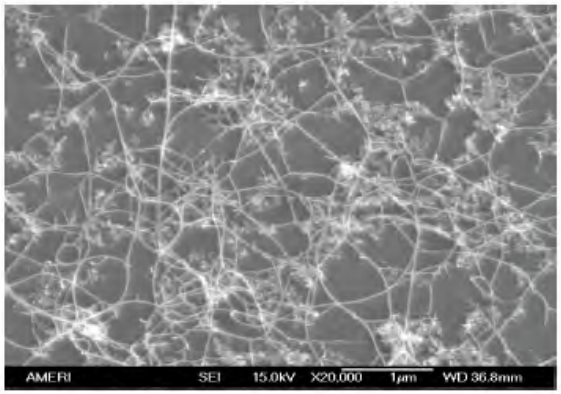
# Carbon Nanotube Based Humidity Sensor

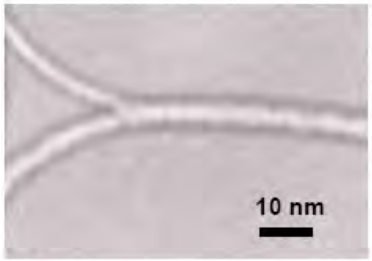



(c)




(d)



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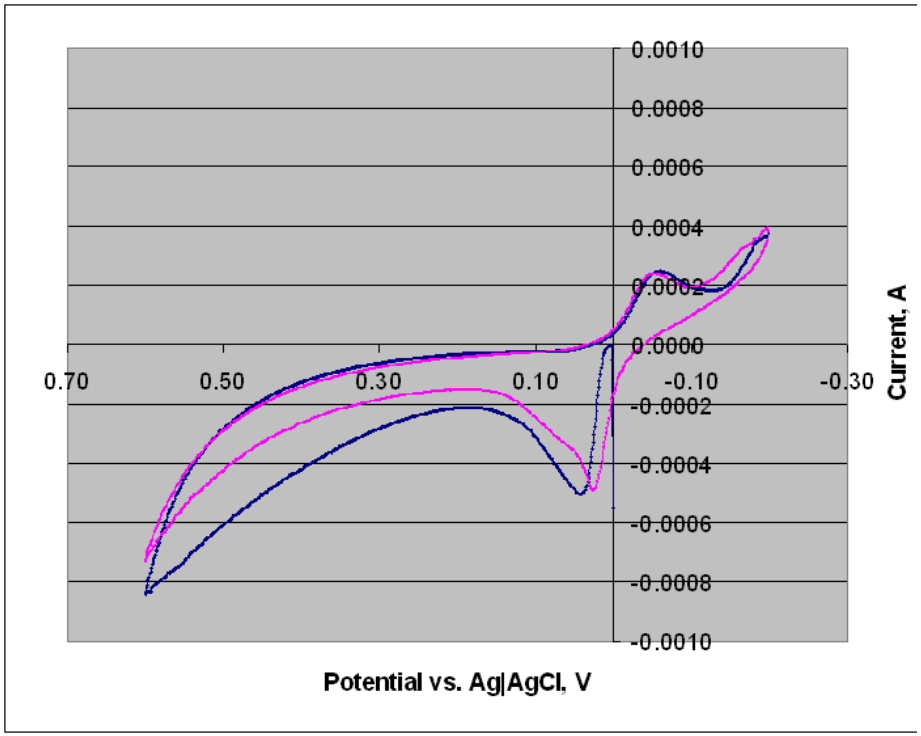
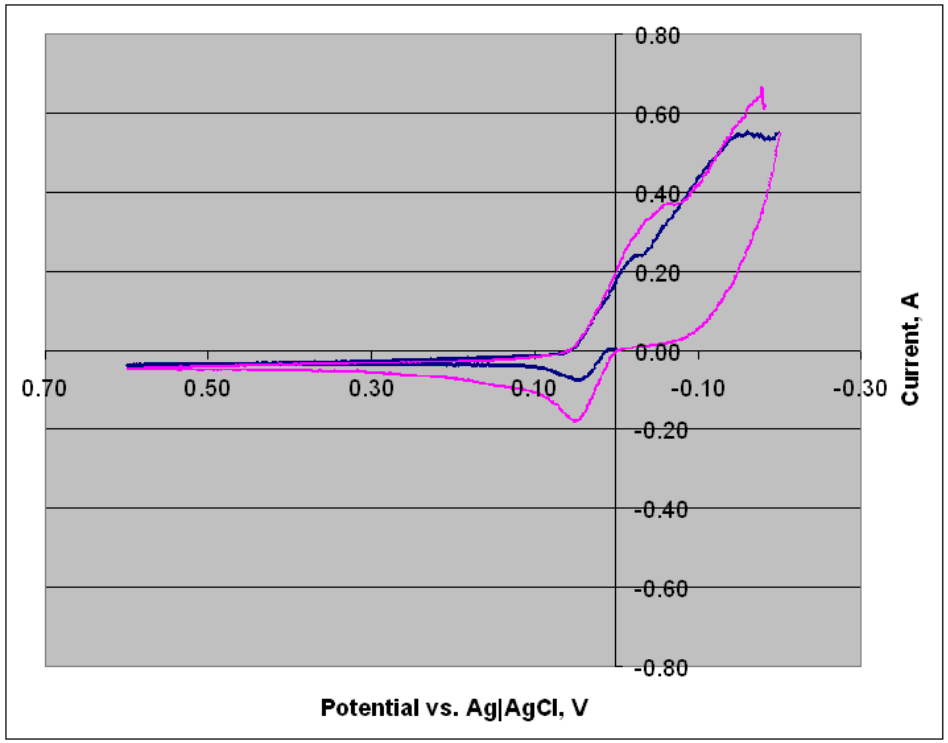
# 2008 Results:
## Mn(II)/Mn(III) Mediator




Original sample

Sulfuric acid treated sample

# 2008 Results:
## Sensitivity of sensors with various mediators

| | $I_{ca}$ (ori) | $I_{an}$ (ori) | $I_{ca}$ (sul) | $I_{an}$ (sul) | $I_{ca}$ (sul)/ $I_{ca}$ (ori) | $I_{an}$ (sul)/ $I_{an}$ (ori) |
|---|---|---|---|---|---|---|
| Ag(I)/Ag(II) | 0.001 | 0.0005 | 0.0125 | 0.006 | 12.5 | 12 |
| Mn(III)/Mn(IV) | 0.0004 | 0.00081 | 0.65 | 0.18 | 1625.0 | 222.2 |
| Ce(III)/Ce(IV) | 0.015 | 0.042 | 0.026 | 0.045 | 1.733 | 1.071 |
| Cu(I)/Cu(II) | 0.0055 | 0.0125 | 0.145 | 0.05 | 26.36364 | 4.0 |

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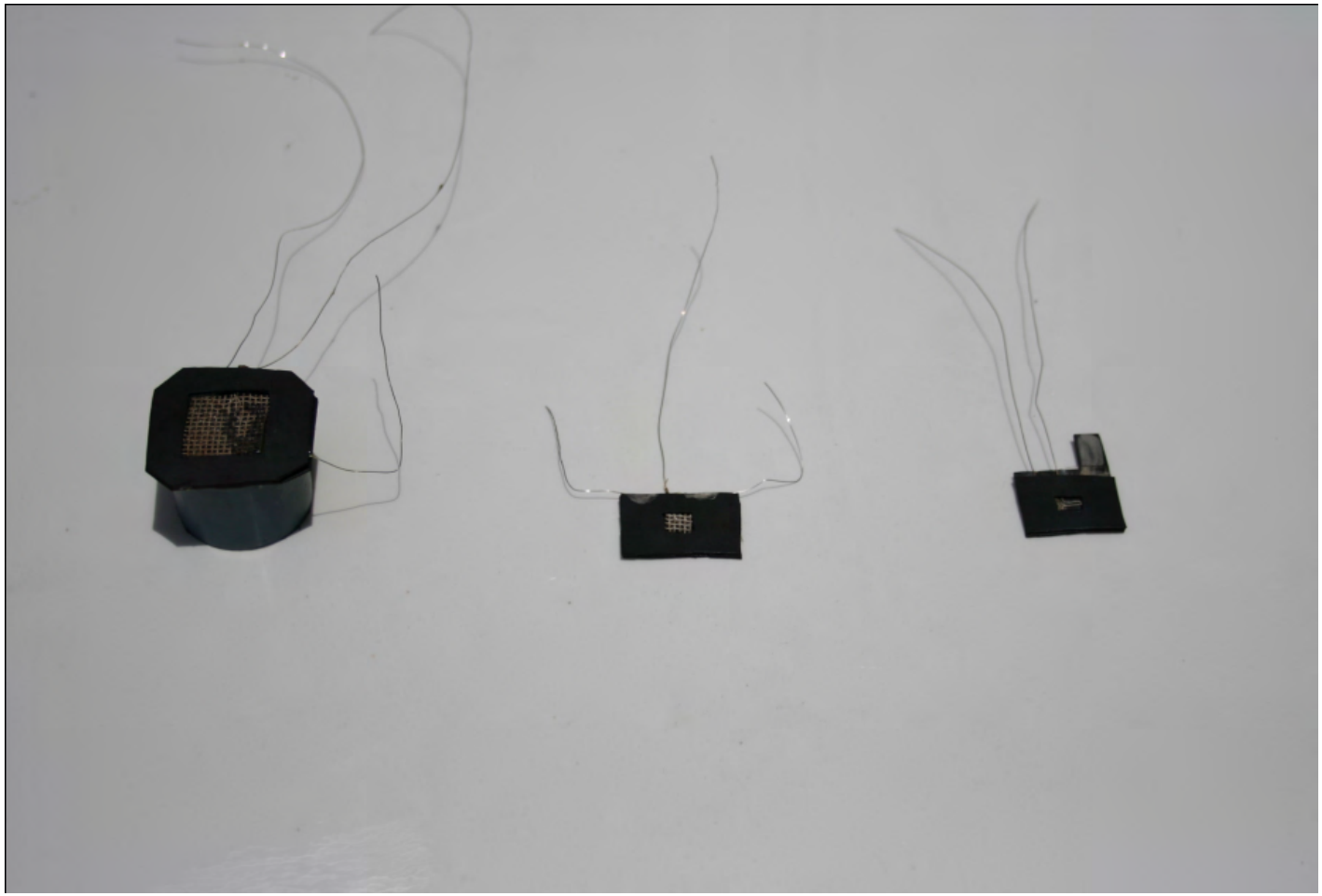
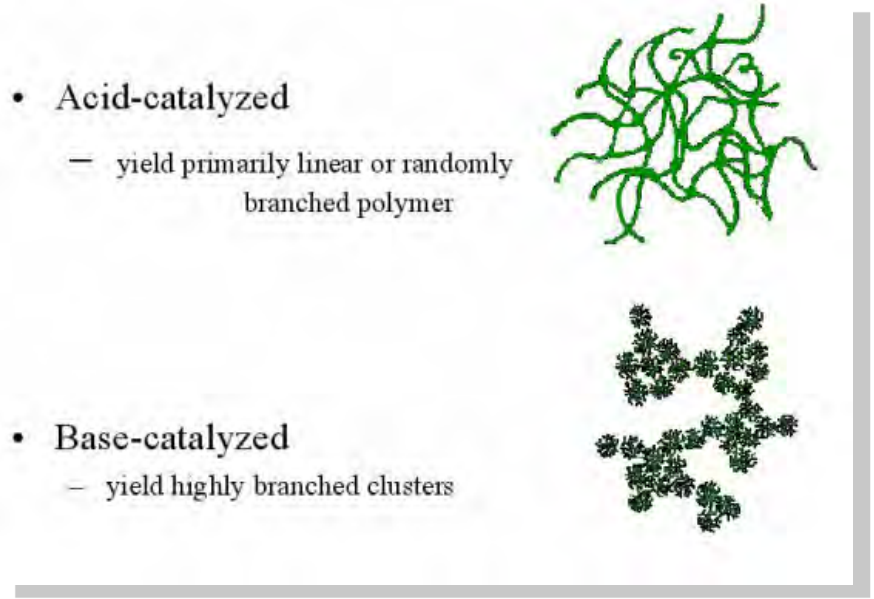
# Prototype Sensor



# New Solid-State Electrolyte

**The formation of silica networks using sol gel method in Nafion electrolyte can increase the mechanical and chemical stability and durability, promote conductivity, and reduce leaching of mediator that causes degradation of the sensor.**



# Protocol for Synthesis

**TEOS+EtOH** **HCl+EtOH+$H_2O$**

**60°C Stirring 4h** **I+NaI+nafion117 solution**

**Nafion117** **$SiO_2$ sol-gel**

**Nafion/(I/NaI)/$SiO_2$ mixed solution**

**RT 48 hours**

**Nafion/(I/NaI)/$SiO_2$ Composite membrane**

# Characterization Results

Water uptake and conductivity of membrane samples

| Sample | Conductivity (S/cm) | Water uptake |
|---|---|---|
| Cast Nafion film | $0.75 \times 10^{-3}$ | Disintegrate in water |
| 60C1 (sol-gel+Nafion) | $0.236 \times 10^{-3}$ | 32% |
| 60C5(sol-gel+Nafion) | $0.376 \times 10^{-3}$ | 27% |
| 60C10(sol-gel+Nafion) | $0.476 \times 10^{-3}$ | 15% |
| 85C1(sol-gel+Nafion) | $0.265 \times 10^{-3}$ | 32% |
| 85C10(sol-gel+Nafion) | $0.220 \times 10^{-3}$ | 27% |
| 85CST1(sol-gel+Nafion) | $0.159 \times 10^{-3}$ | 15% |
| ISN1 (sol-gel+Nafion+mediator) | 0.0102 | |
| ISN2 (sol-gel+Nafion+mediator) | 0.0976 | |
| ISN3 (sol-gel+Nafion+mediator) | 0.1075 | |

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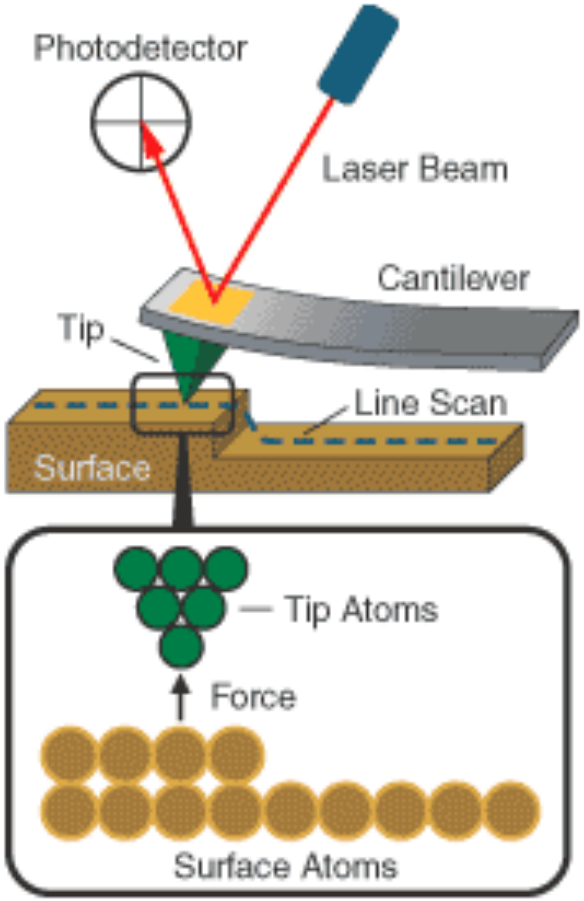
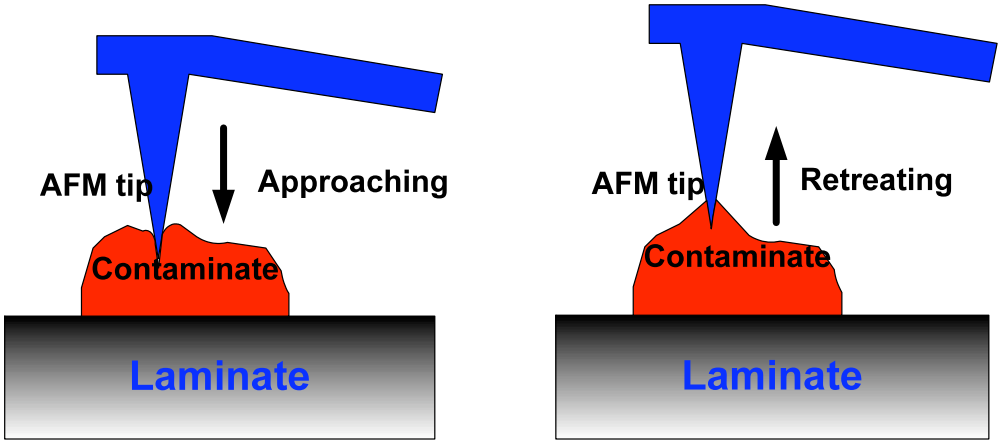
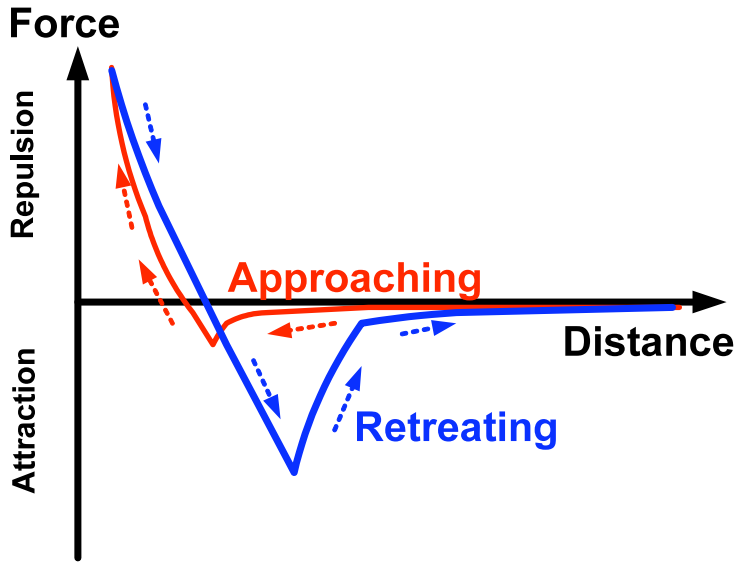
# Review of Atomic Force Microscopy (AFM)



# Review of Force Spectroscopy



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# Previous Analyses

- AFM – studies were conducted in both tapping and contact modes - tapping mode offers a better result to identify contamination.
- Force Spectroscopy – variations suggest modified tip probe may offer better results for identifying contamination.
- CFM – motivated by analyzing surface activity. Obtained images for hydroxyl modified probes. Best results are likely with the epoxy functional group modified probes.

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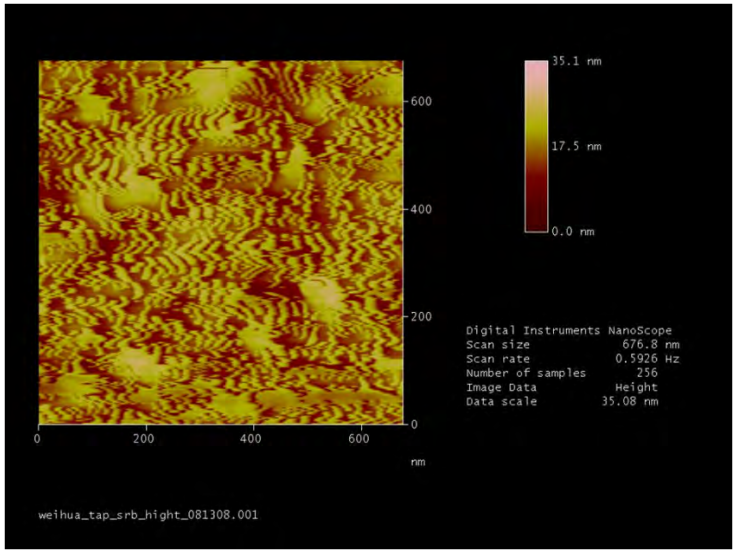
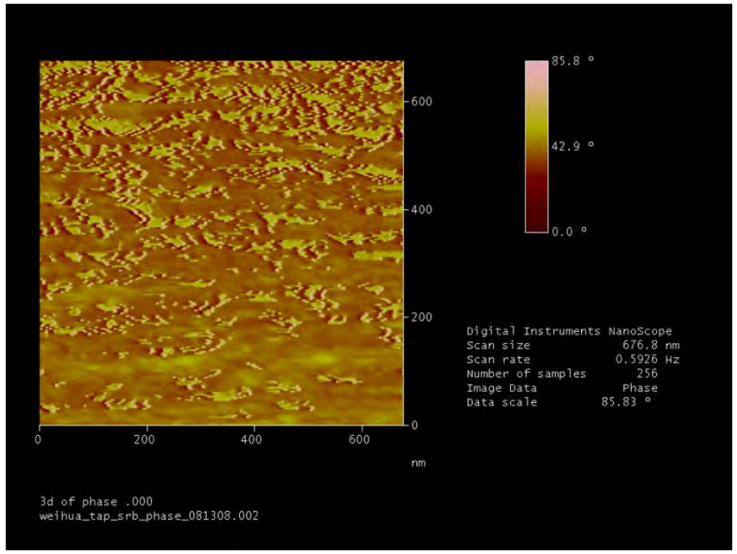
# SRB Prepared Composite AFM Image (Tapping Mode)

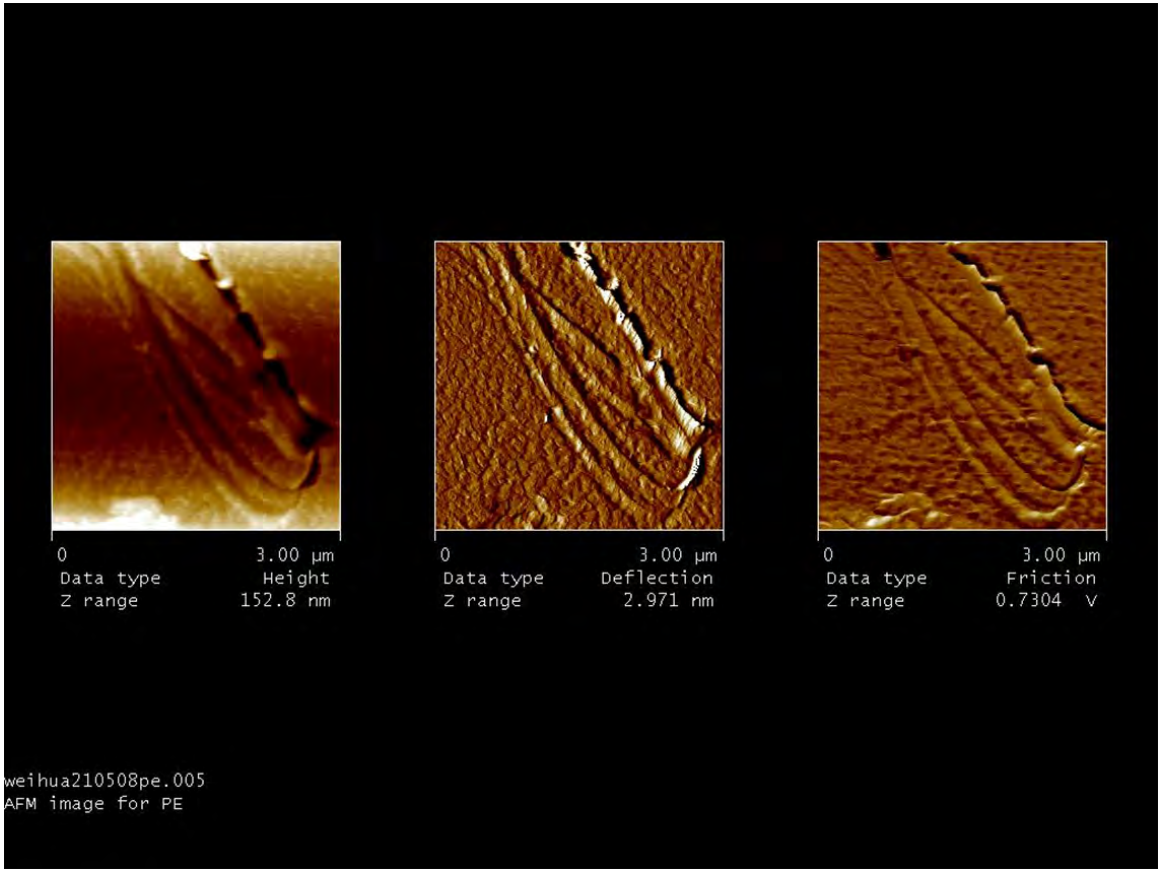



Height image




Phase image

# PE Prepared Composite Images Under Contact Mode



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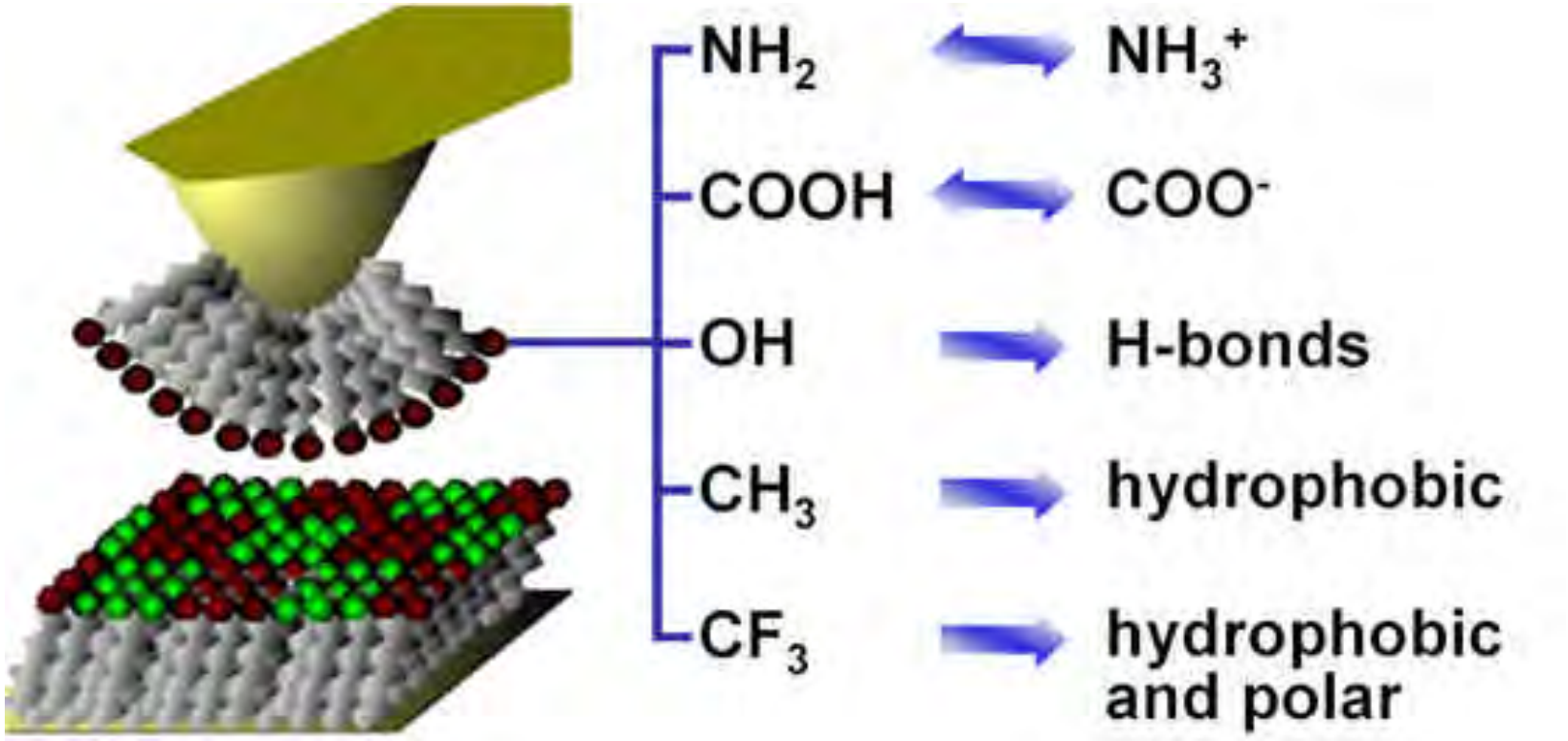
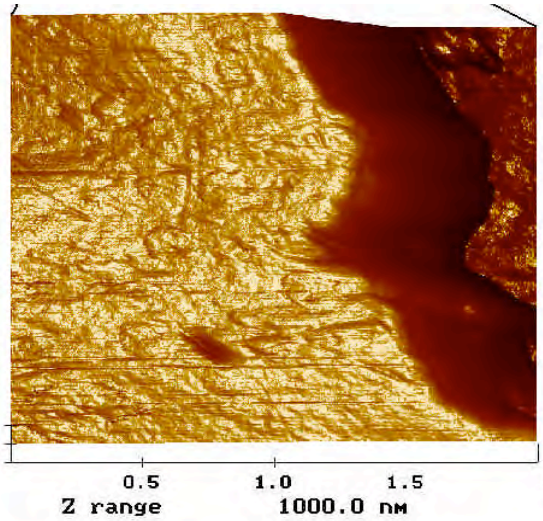
# Review of Chemical Force Microscopy

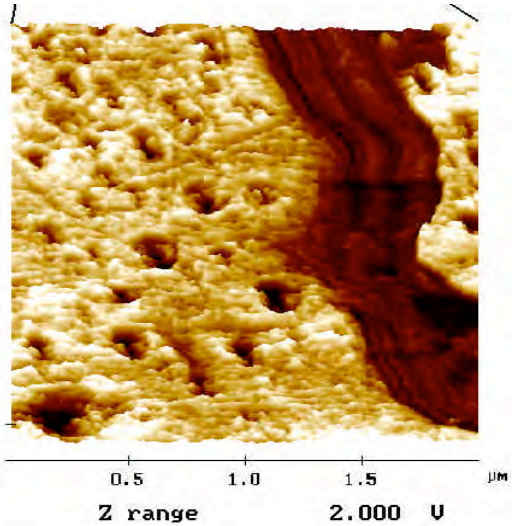
Chemical properties on surface



# Strategy for Mapping Chemical Surface Properties (Surface Activity) with CFM




**Height image of sample surface**




**Friction image of sample surface**

Notable differences between the height and friction images include the dark circular areas on the friction images which can represent localized contamination.

Comparison between CFM imaging can provide information regarding chemical properties which is relevant to adhesive bonding (i.e. Frisbie, et. al, *Science*, 1994,**265**:2071, Poggi, et. al, *Nano Letters*, 2004, **4**:61).

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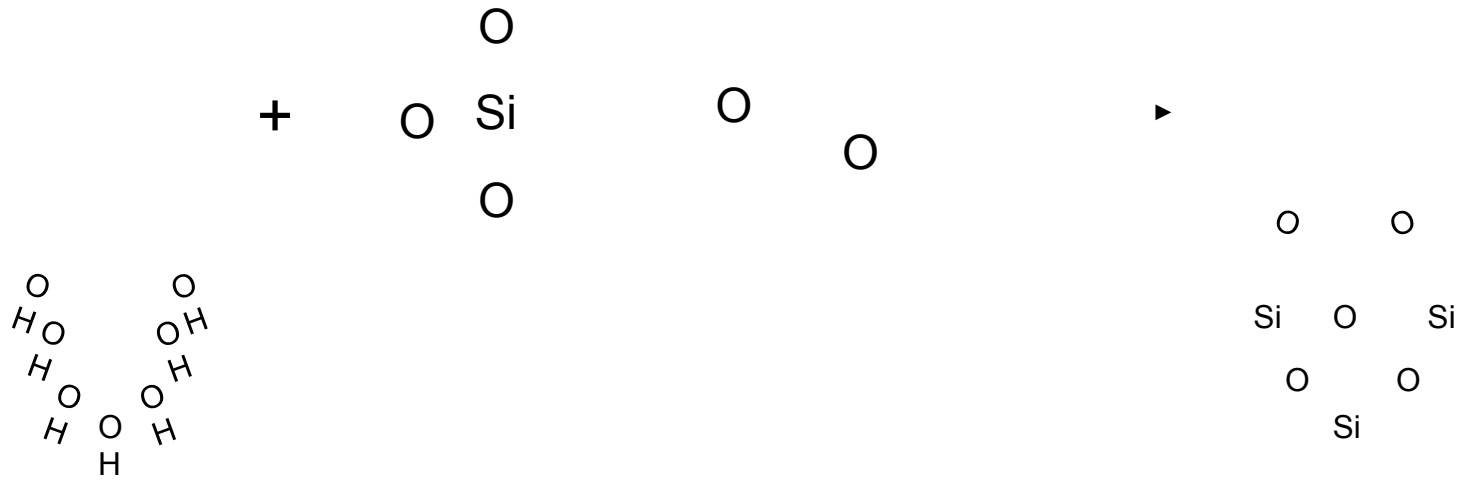
# Mapping Active Sites Using Epoxy Functional Group Modified CFM Probe

- Interactions between composites and epoxy resin are important for bonding strength.
- No prior use of an epoxy group modified probe has been recorded according to our literature review. Epoxy group modified probes are not available commercially, this study is the first research effort that seeks to synthesize an epoxy functional group modified probe.
- CFM with epoxy functional group modified probe will mimic the interactions between composite surfaces and epoxy resin adhesives.
- Both contact and tapping modes will be used to map the chemical properties on composite surfaces.

# Strategy for Immobilization of Epoxy Functional Group on Probe



Silicone or $SiN_4$ AFM probe

3-Glycidoxypropyl-trimethoxysilane (GPS)

Epoxy modified AFM tip

# A Look Forward

- Benefit to Aviation
  - Better understanding of the pre-bond surface preparation methods
  - Better understanding of bond strength and durability versus surface preparation
  - Novel in-field, online certification and assurance technology for surface preparation
  - Reduced costs for surface preparation and adhesive bonding processes
- Future needs
  - In-field, online analytical detection and monitoring technologies for manufacture, chemical, environmental, and energy industries.

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# Thank you!

Hard Questions:

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