Nanoscale Photoswitchable Surfaces

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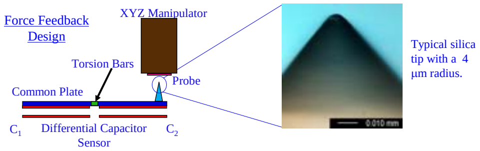
Goals: Combine surface photochemistry and nanoscale morphology to understand and develop a new generation of microfluidic devices for chem/bio sensing applications for national security, environmental and biological assays, proteomics, etc.
CINT Capabilities: Surface and interface characterization instrumentation (IFM* and surface spectroscopy) and also micro/nanofluidics fabrication (future).

*CINT facilities used for the present research are the Interface Force Microscopes (IFMs).

Background

Approach

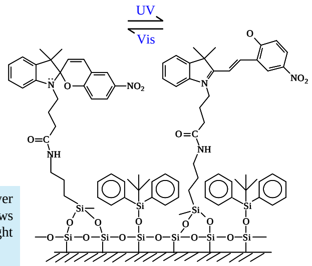
Use the Interfacial Force Microscope (IFM) to directly observe at the nanoscale and gain new insight into the optical photoswitching of Self Assembled Monolayers (SAMs) on surfaces. The CINT IFM enables the quantitative mapping of the entire force-distance profile as a tip approaches a substrate surface, without the mechanical instabilities that can plague other interaction force measurements.



Typical silica tip with a 4 µm radius.

Surface Design of Photochromic Monolayers

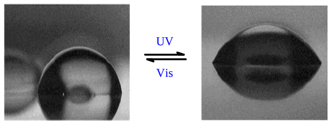
The photoswitchable molecule is bound to the surface by reacting the carboxylic acid end of the functionalized spiropyran with a SAM created using 3-aminopropyldiethoxymethylsilane to form a covalent amide linkage. Because the extent and kinetics of the photoactivation are sensitive to the local spiropyran environment the amide-linked spiropyrans are diluted to ~20% with *tert*-butyldiphenylsilyl groups as spacers for optimum switching.



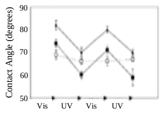
A schematic of spiropyran monolayer on glass or oxidized Si surface shows the closed (left side) and open (right side) states.

Reversible Light Switching of Macroscopic Spiropyran Surface Properties

Spiropyran coated surfaces allow for manipulation of its surface energy, wetting, and fluid flow characteristics.



Example of water drops on a photosensitive surface using UV and Vis radiation.



Light induced change in water contact angle on coated slides.

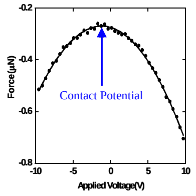
R. Rosario, D. Gust, M. Hayes, F. Jahnke, J. Springer, and A. A. Garcia, "Photon-Modulated Wettability Changes on Spiropyran-Coated Surfaces" Langmuir, *18*, **2002**, 8062.

Previous Studies

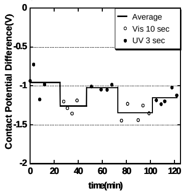
Contact Potential Measurements

The change in surface states induced by photoactivation of the spiropyran is obtained using contact potential measurements to probe the polarity of the monolayer.

Surface polarity photoswitches, with spiropyran dipole pointing toward the surface on ring opening.



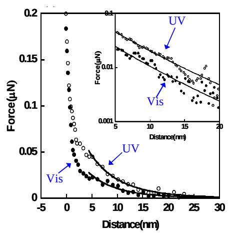
Force response at 20 nm from the surface in air as a function of applied voltage between the Au coated tip (at ground) and the monolayer surface.



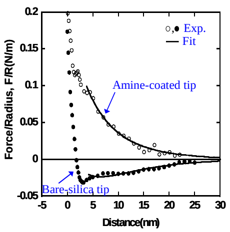
Contact potential switching behavior of spiropyran between open and closed forms after UV & Visible light exposure.

IFM Force Profiles on Spiropyran Coated Surfaces

IFM normal force profile (dots) and theoretical fits (solid lines) taken with an amine coated tip after exposure to UV or visible light (spiropyran surface under high dielectric formamide containing 2 mM KCl):



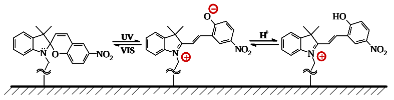
Surface charge density determined to be 0.028 C/m² after UV exposure and 0.014 C/m² after exposure to visible light. Inset is the log scale plots of data and fits.



Force normalized by tip-radius after UV exposure taken with an amine-coated and bare silica tip demonstrate the spiropyran surface is positive when exposed to UV.

Spiropyran protonation

IFM force profiles show that ~10 to 20% of the spiropyran are protonated upon ring opening in electrolyte solutions, amplifying the switching of electrical double-layer forces.



Spiropyran in the closed state (left) and the open states before (middle) and after (right) protonation. When the pyran ring opens, the phenoxy anion in the open ring can be protonated to form a phenol. This results in converting the neutral molecule dipole into a positively charged entity.

B. Bunker, B. I. Kim, J. E. Houston, R. Rosario, A. A. Garcia, M. Hayes, D. Gust, and S. T. Picraux, "Direct Observation of Photo Switching in Tethered Spiropyrans Using the Interfacial Force Microscope" Nano Letters, *3*, **2003**, 1723.

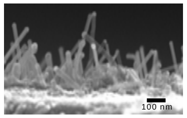
New Surfaces for Investigation at CINT

Si Nanowire Surfaces

The fractal dimension of the Si nanowire surface was determined to predict the contact angle change between smooth and rough surfaces.

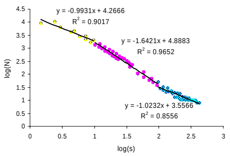
$$\cos\theta_{rough} = \left(\frac{L}{l}\right)^{D-2} \cos\theta_{smooth}$$

FESEM of Si nanowire surface



Profile of Si nanowire surface

Box fitting analysis



Fractal Parameters

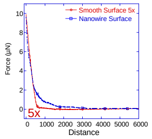
D	*l (nm)*	*L (nm)*
2.64	12	94

The cross sectional fractal dimension (D) was found to be 2.64. The values of the lower and upper limits of fractal behavior were 12 nm and 94 nm, respectively

IFM Comparison of Smooth and Rough Surfaces

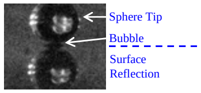
Force profiles collected during a CINT visit indicate a dramatic difference between the smooth and rough surfaces.

IFM Force Profiles



IFM force profiles on smooth and rough (nanowire) surfaces in air.

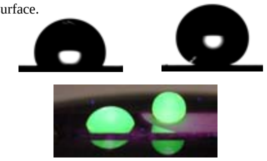
Superhydrophobic surface nucleates gas bubble in IFM



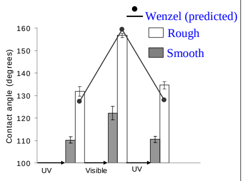
The fluorinated nanowire surface is so hydrophobic that under water, bubbles form when the IFM tip approaches, similar bubble formation is not observed on the smooth surface.

Combine Surface Morphology and Chemistry to Amplify Photoswitching

The combination of fractally rough nanowire surfaces and a hydrophobic coating resulted in significantly higher contact angles on the nanowire surface compared with the smooth surface.



Top: Water drops on surfaces with identical spiropyran coatings irradiated with visible light. Bottom: Dyed drops on identical spiropyran coatings irradiated with UV light. Both: Smooth surface (left) and rough surface (right).



Advancing contact angle changes on smooth and rough photoresponsive surfaces under UV and visible light irradiation.

R. Rosario, D. Gust, A. A. Garcia, M. Hayes, J. L. Taraci, T. Clement, J. W. Dailey and S. T. Picraux "Lotus Effect Amplifies Light-Induced Contact Angle Switching" J. Phys. Chem. B., *108*, **2004**, 12640.

Conclusions

- The IFM provides valuable nanoscale characterization of surface photoswitching.
- Rough nanowire morphology results in amplification of contact angle switching.
- First motion of water droplets on surface using only a light gradient, opening the door to enhancement of liquid motion in surface-tension driven microfluidic systems.

*Postdoc, +Graduate Student
CINT Proposal Number
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