# CHIMICA DELLE SUPERFICI ED INTERFASI

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LAUREA MAGISTRALE IN INGEGNERIA CHIMICA

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# OUTLINE

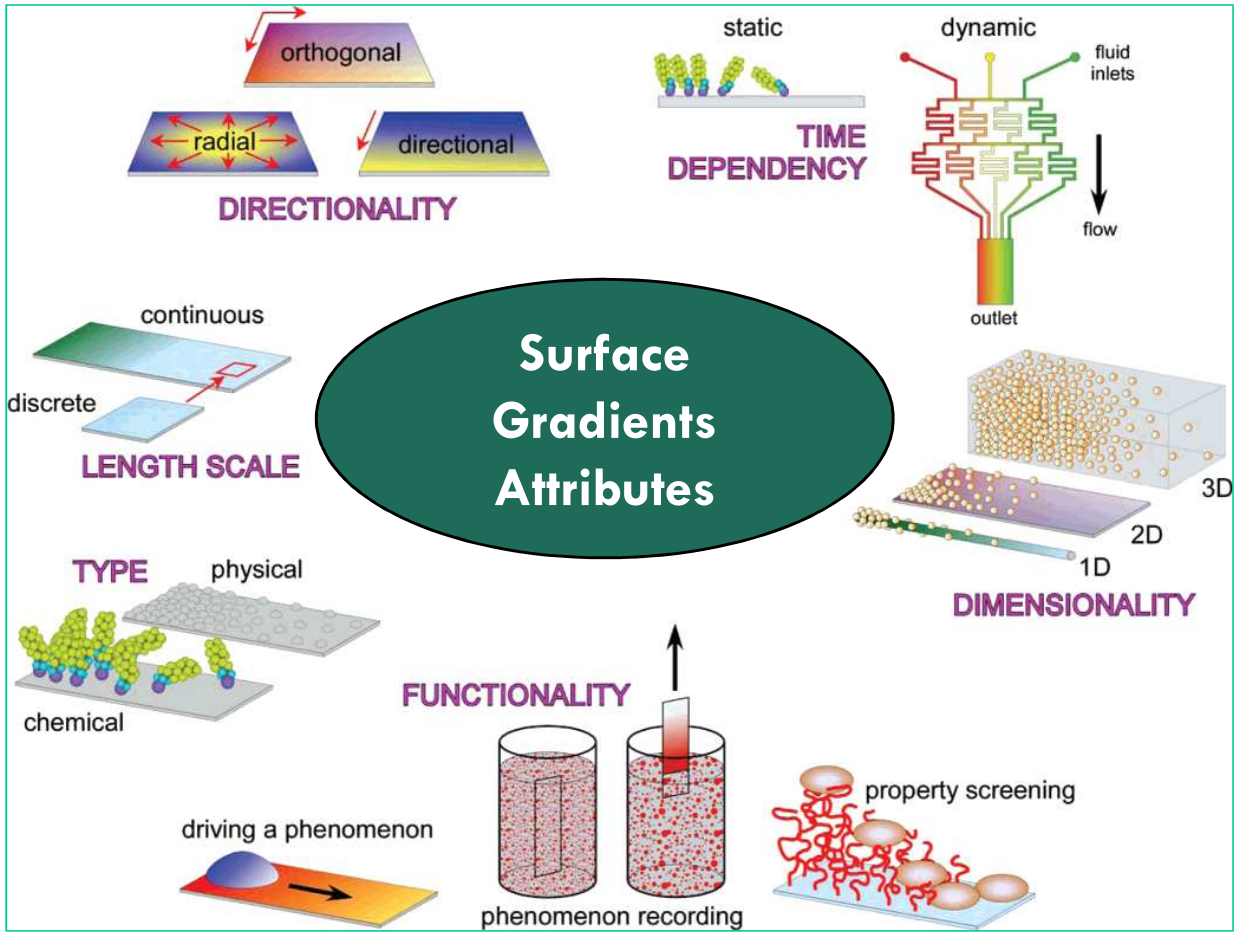
- SURFACE CHEMICAL GRADIENTS
- DROPLET MOVEMENT ON WETTABILITY GRADIENT
- WETTABILITY GRADIENT FORMATION
  - SILANES GRADIENT ON SI
  - THIOLS GRADIENT ON AU BY WITHDRAWING EC DESORPTION

# SURFACE GRADIENTS PROPERTIES

THE SURFACE PHYSICAL AND CHEMICAL PROPERTIES CHANGE CONTINUOUSLY ALONG THE MATERIALS.

- PHYSICOCHEMICAL NATURE
- DIMENSIONALITY (1D, 2D, 3D)
- DIRECTIONALITY (UNIDIRECTIONAL, ORTHOGONAL OR RADIAL)
- LENGTH SCALE (CONTINUOUS OR DISCONTINUOUS)
- TEMPORAL DEPENDENCY (STATICAL OR DYNAMICAL)
- FUNCTIONALITY

# SURFACE GRADIENTS




Genzer et al. 2008, Langmuir, 24, 2294-2317

# SURFACE-CHEMICAL GRADIENT APPLICATIONS

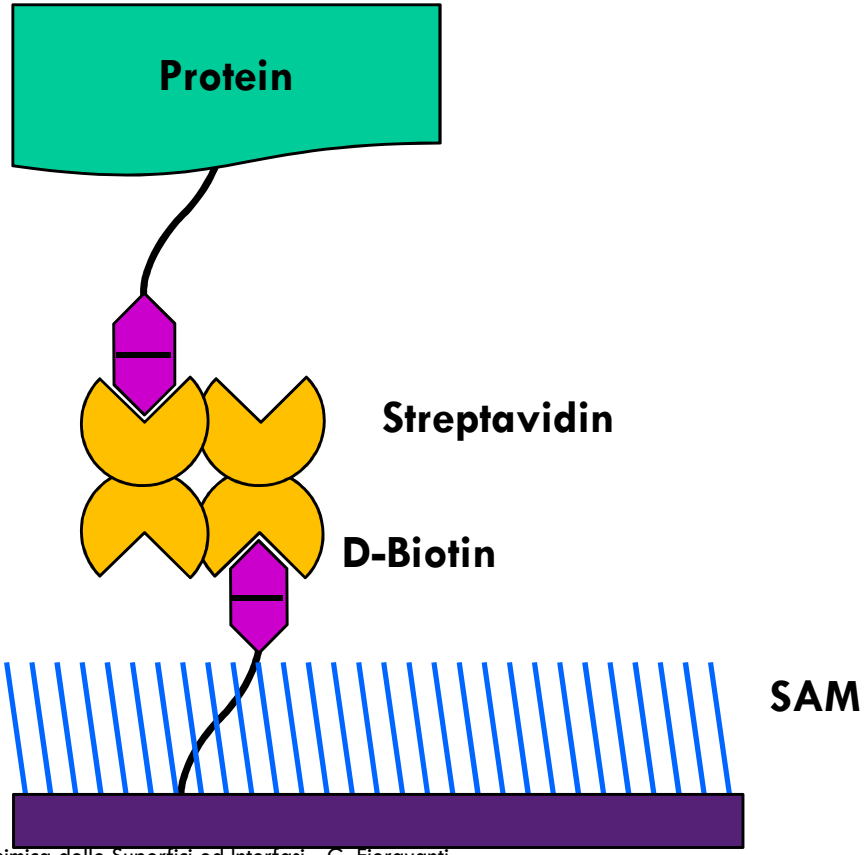
SMART RESPONSIVE MATERIALS

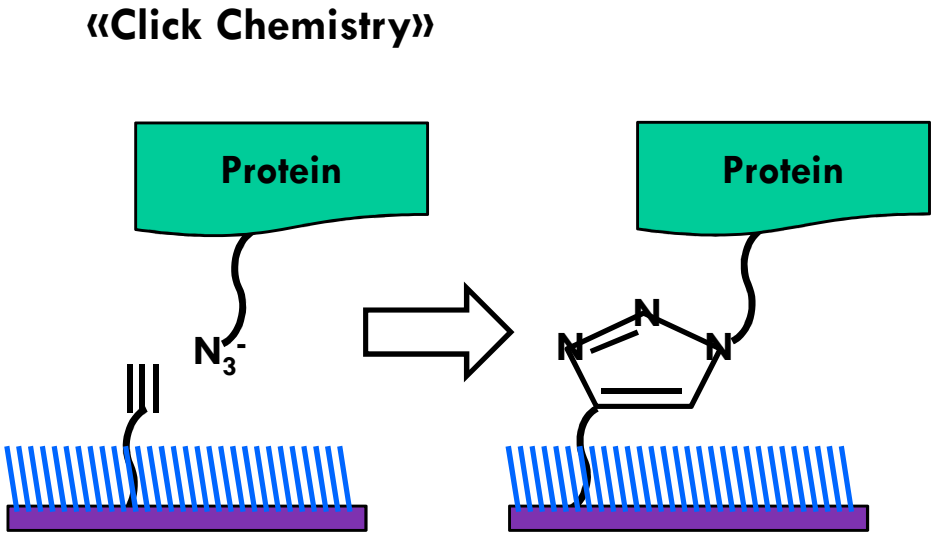
- DRIVING
- RECORDING
- SCREENING (PHYSICOCHEMICAL PHENOMENA)

BIOLOGYCAL APPLICATIONS

- CELL ADHESION
- PROTEIN ADSORPTION
- CELL GROWTH

# SURFACES BIOFUNCTIONALIZATION



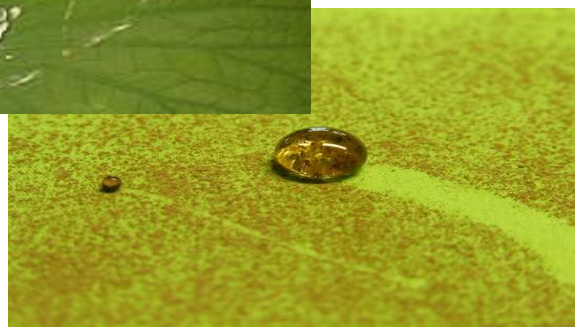



# WETTABILITY GRADIENT

CHEMICAL HETEROGENEITY AND SURFACE ROUGHNESS

(MICRO/ NANO SCALE)

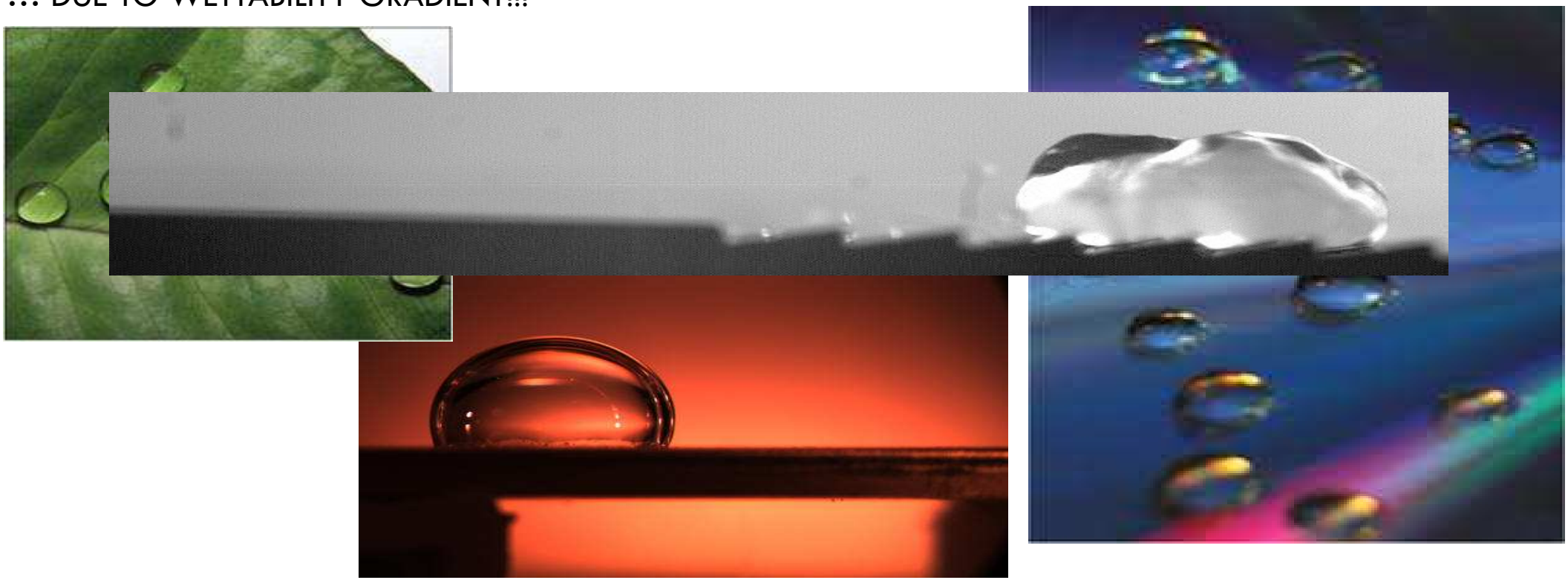
**Lotus leaf effect**



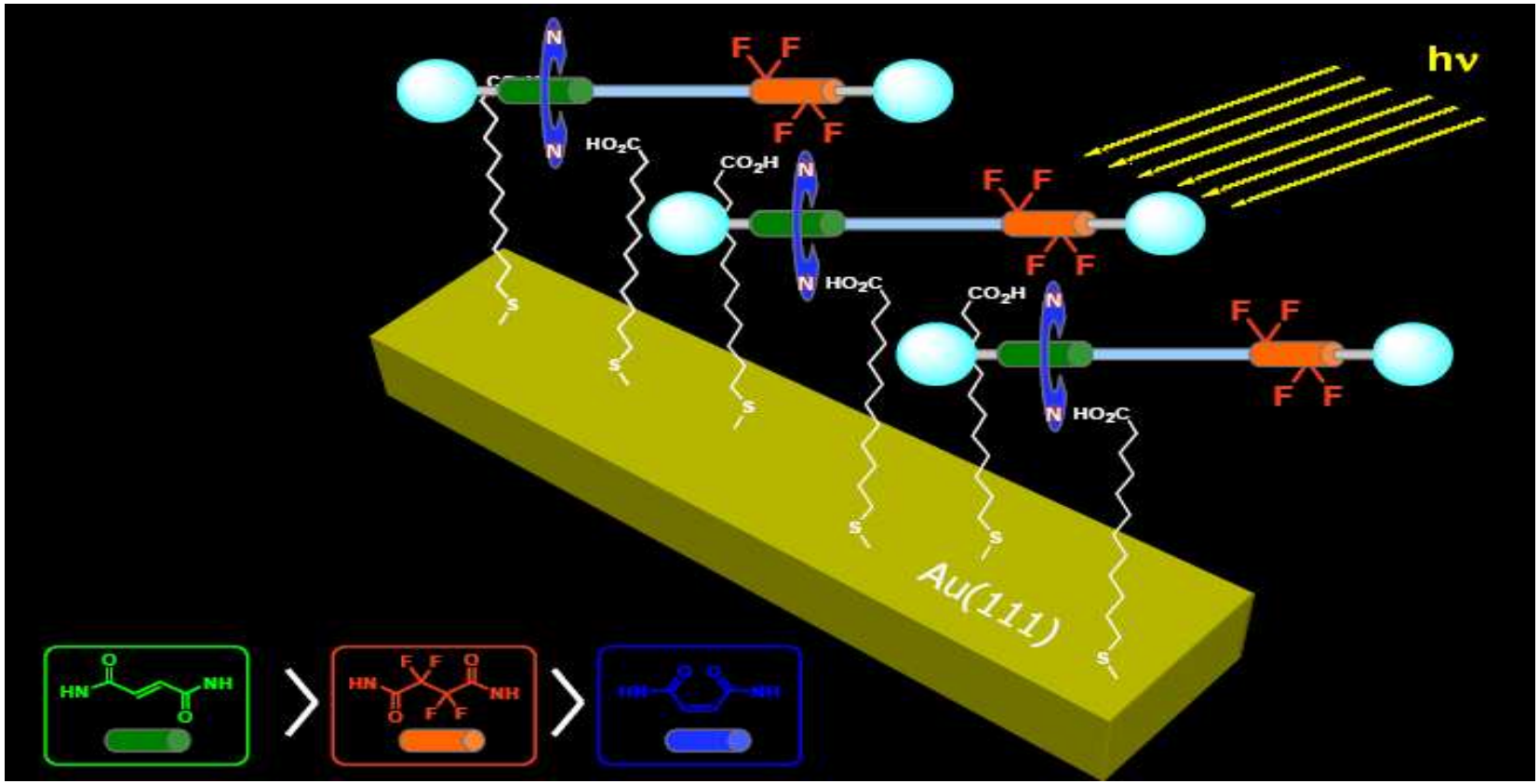
**Superhydrophobic surfaces**

# MAIN GOAL: DROPLETS MOVEMENT

… DUE TO WETTABILITY GRADIENT!!!



# BENZYLIC AMIDE ROTAXANES

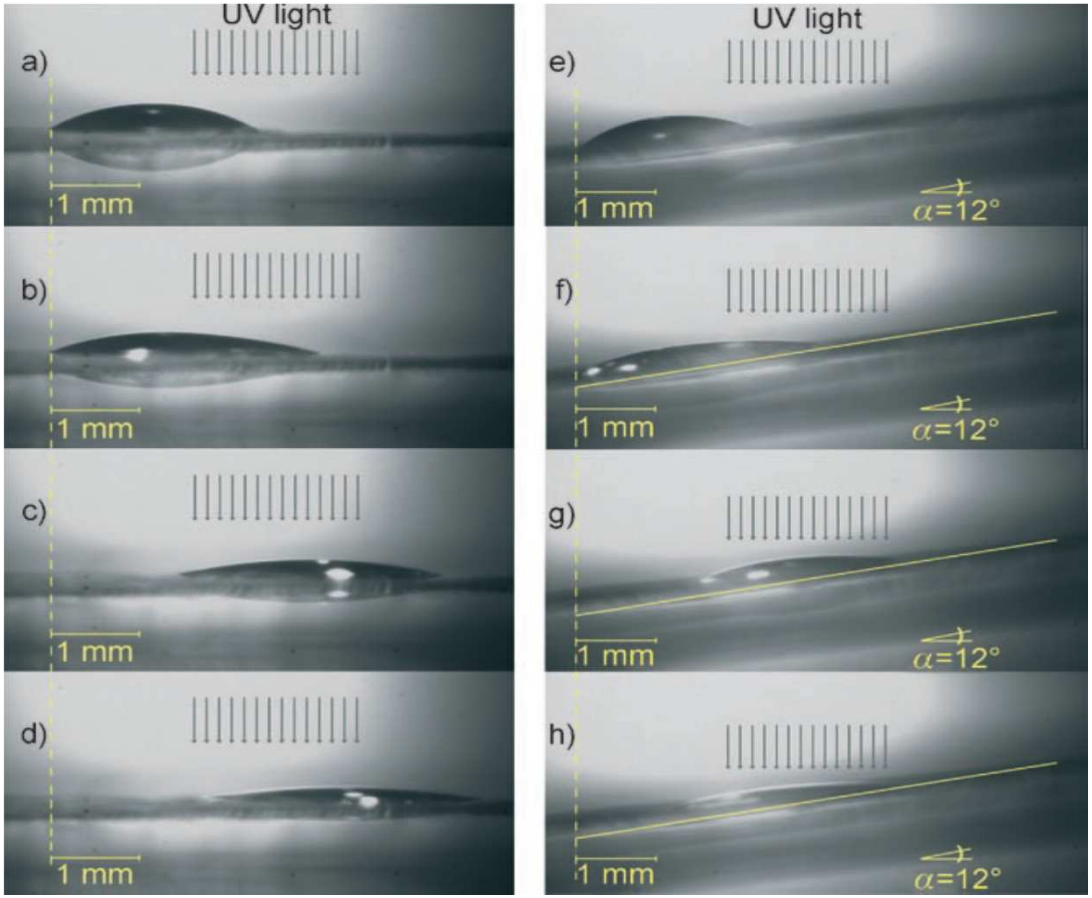





Nature Mat., 2005, 4, 704

# TRANSPORT ON SURFACE

UV-LIGHT ISOMERIZES THE FUMARAMIDE STATION, CAUSING THE DISPLACEMENT OF THE MACROCYCLE, WHICH CONCEAL THE FLUOROALKANE UNITS LEAVING A MORE POLAROPHILIC SURFACE




Nature Mat., 2005, 4, 704

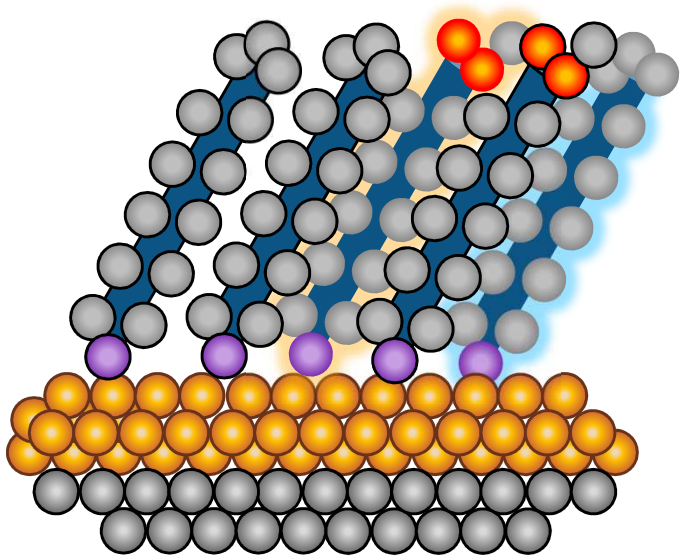
# SURFACE-CHEMICAL GRADIENT PREPARATION TECHNIQUES

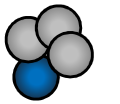
| Technique | | Adsorbate | Substrate |
|---|---|---|---|
| **Diffusion** | Vapour phase | Silanes | Si, PDMS |
| | Solvent | Silanes | Si |
| | Through a matrix | Alkanethiols, Silanes | Au |
| **Printing** | Contact | Alkanethiols, Silanes | Au, Si (also functionalized) |
| | Ink jet | Alkanethiols, Silanes | Au, Si |
| **Advancing solution** | Concentration gradient | Monomers, Proteins | Au, Si (also functionalized) |
| | Controlling reaction time | Alkanethiols, Silanes | Au, Si |
| | Depletion | Proteins | PDMS, Glass |
| **Irradiation** | Intensity, exposure time, mask | Silanes, Alkanethiols, Monomers, Proteins | Au, Si (also functionalized) |
| **Controlled polymerization** | Temperature, plasma or electropolymerization | Alkanethiols, Monomers | Au |
| **Desorption** | By potential or irradiation | Alkanethiols | Au |

# WETTABILITY GRADIENT BY MIXED SAM APPROACH

# WHAT MEANS "MIXED SAM"?

TWO DIFFERENT FUNCTIONALITY (HYDROPHOBIC, HYDROPHILIC) WITH DIFFERENT DENSITIES ALONG THE SURFACE.





**Head group = $CH_3$**

**Head group = COOH**

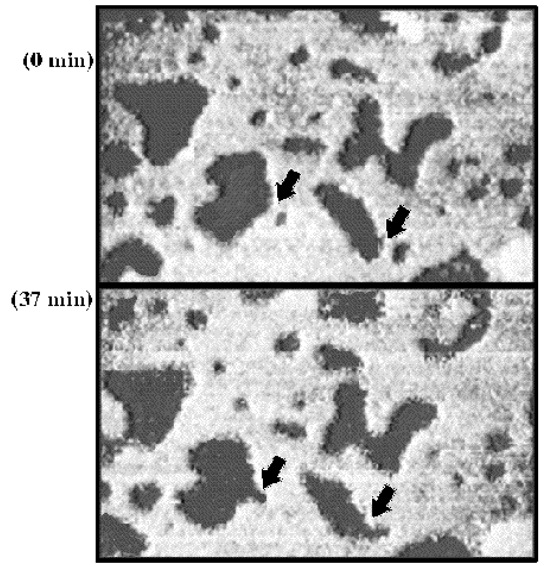
# MIXED SAM FORMATION

1. **KINETIC CONTROL**: THE MOLECULES IN SOLUTION REACH RANDOMLY THE METAL SURFACE AND BIND IRREVERSIBLY TO IT. THE RESULT OF THIS PROCESS LEADS TO THE FORMATION OF AN ORGANIC MATRIX IN WHICH THE TWO COMPONENTS ARE ARRANGED RANDOMLY, IN SUCH PROPORTION AS TO REFLECT THE COMPOSITION OF THE STARTING SOLUTION.
2. **DIFFUSION MECHANISM**: THE IRREVERSIBLE CHEMISORPTION IS FOLLOWED BY A DIFFUSION AT THE SURFACE WHICH RESULTS IN A REDISTRIBUTION OF THE ADSORBATES, TO GIVE A FINAL SITUATION IN WHICH THEY ARE ARRANGED IN THE WAY THAT BEST SUITS THEM (ALBEIT LIMITED BY THE CONSTRAINTS IMPOSED BY THE KINETIC PHASE INITIAL ADSORPTION).

# MIXED SAM FORMATION

3. **EXCHANGE MECHANISM**: ADSORPTION IS NOT AN IRREVERSIBLE PROCESS, BUT A DYNAMIC ONE: AFTER A FIRST STATISTICS ARRANGEMENT, THE CONTINUOUS PROCESSES OF ADSORPTION AND DESORPTION REQUIRE ACHIEVEMENT OF A FINAL THERMODYNAMIC EQUILIBRIUM, GENERALLY REPRESENTED BY THE FORMATION OF DOMAINS OF MOLECULES OF THE SAME KIND.

Two sequential STM images taken 37 min apart showing a SAM containing islands of $CH_3(CH_2)_{15}S$- (topographically lower, shown as darker) surrounded by $CH_3OCO(CH_2)_{15}S$- (topographically higher, shown as brighter) areas. The SAM was formed from a solution of 75% $CH_3OCO(CH_2)_{15}SH$/25% $CH_3(CH_2)_{15}SH$ on Au{111}. Domain coalescence is observed at this time scale (indicated by the two arrows). The reverse process (one large domain separating into two smaller ones) was not observed.

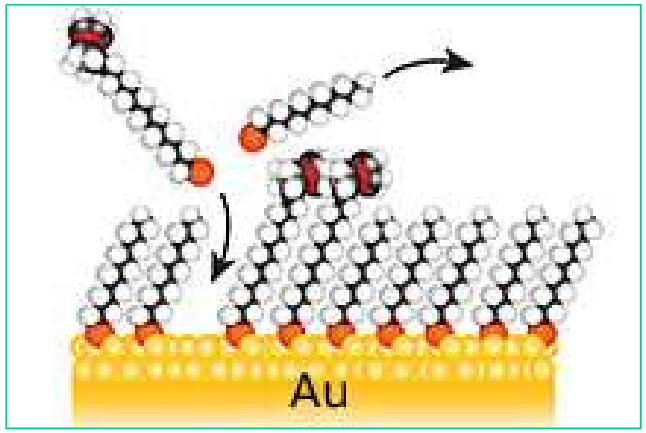


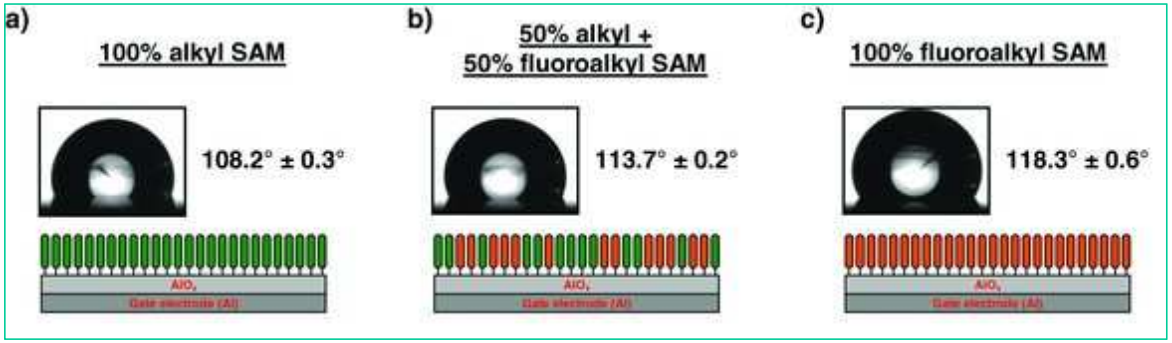

Stranick et al., J. Phys. Chem. 1994,98, 76367646

# MIXED SAM FORMATION

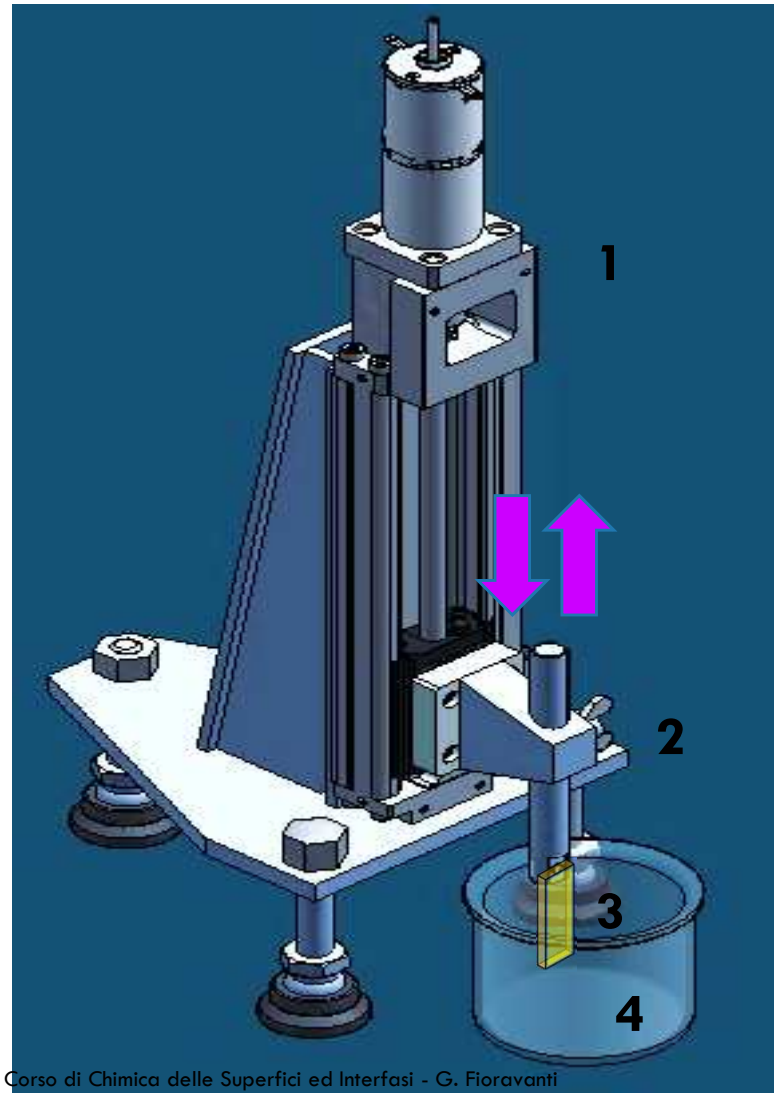
SIMULTANEOUS DEPOSITION VERSUS CONTROLLED DEPOSITION.

TYPICALLY, SOLUTION PROCESSING AND THE SAME ANCHOR CHEMISTRY ENABLE FULL CONTROL OF THE SAM COMPOSITION, WHICH DIRECTLY RELATES TO THE STOICHIOMETRIC COMPOSITION OF THE SOLUTION.




Water contact angles measured on a self-assembled monolayer (SAM) of 100% alkyl phosphonic acid (a), on a mixed SAM of 50% alkyl and 50% fluoroalkyl phosphonic acid (b), and on a SAM of 100% fluoroalkyl phosphonic acid
Zschieschang et al, Adv. Mater. 2010, 22, 4489–4493.




# CONTROLLED ADSORPTION

TWO-STEP IMMERSION METHOD

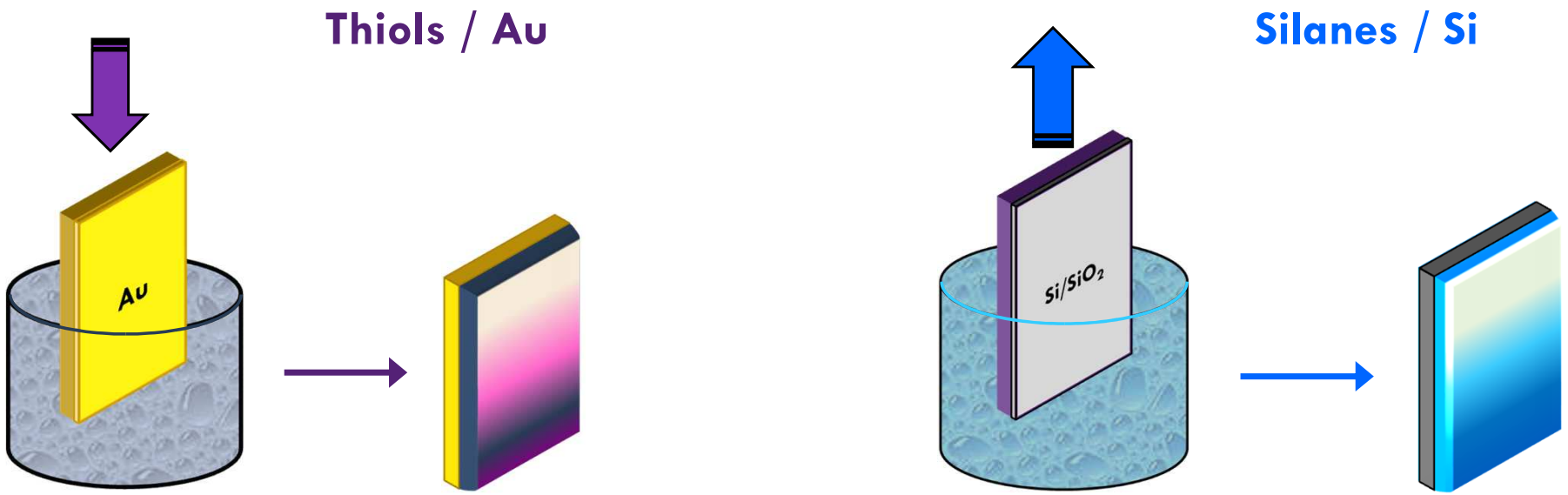
THE FIRST IMMERSION (OR EMERSION) IS PERFORMED BY USING A LINEAR MOTION DRIVE.

1. LINEAR MOTOR
2. SAMPLE HOLDER
3. SAMPLE
4. ADSORBATE SOLUTION 1

Morgenthaler et al. 2003, Langmuir, 19(25), 10459-10462

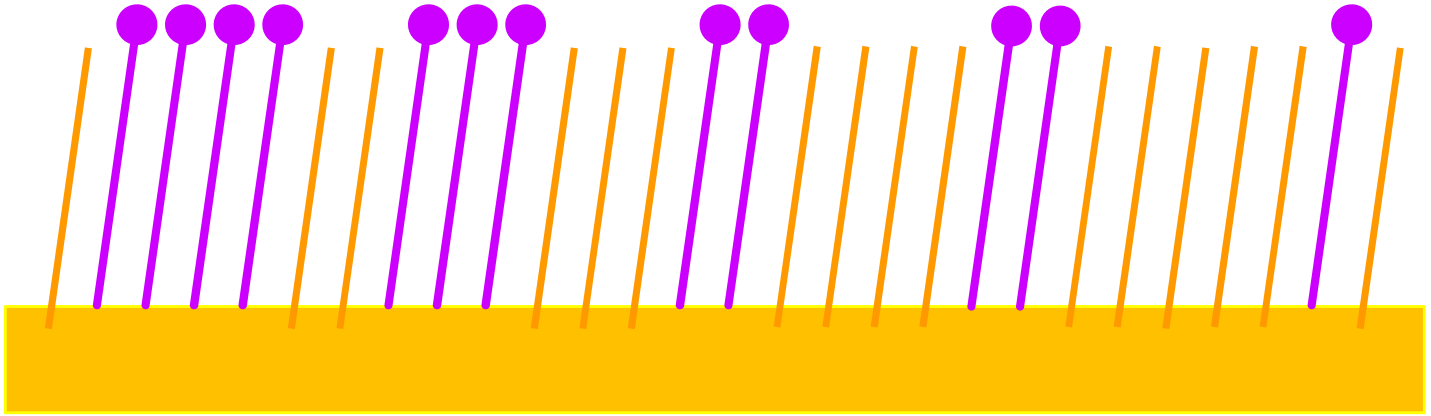
# CONTROLLED ADSORPTION

DIPPING OR UNDIPPING STRATEGY (ADSORBATE 1)



# SECOND STEP

- PARTIAL MONOLAYER
- FULL MONOLAYER (COMPLEMENTARY SAM)



THE SUBSTRATE WAS IMMERSED IN A SOLUTION CONTAINING ADSORBATE 2.

# SAM COMPLEMENTARI

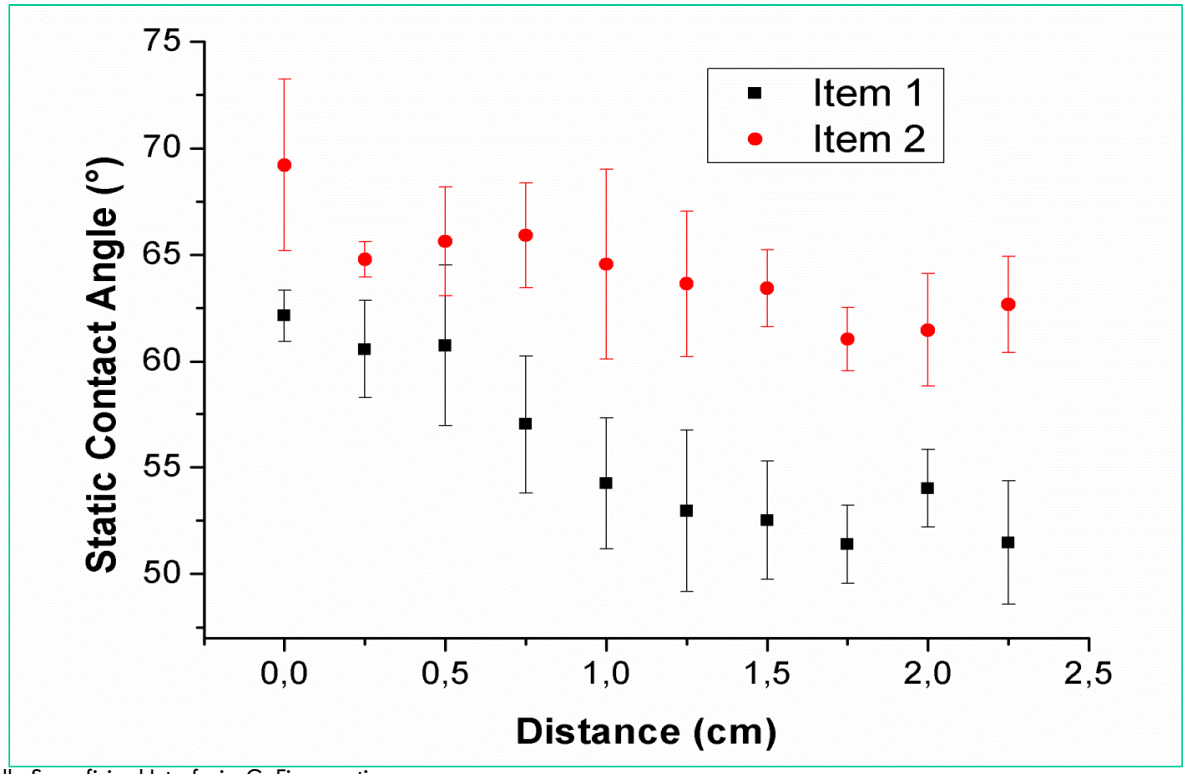
| Substrate | Adsorbate 1 | Type | Adsorbate 2 | Type |
|---|---|---|---|---|
| Au | $CH_3$ thiol | Dodecanthiol | OH thiol | 11-Mercapto-1-Undecanthiol |
| | $CH_3$ thiol | Dodecanthiol | COOH thiol | 11-Mercapto Undecanoic acid |
| Si | $CH_3$ silane | Octadecyltrichlorosilane or Butyltrichlorosilane | - | - |
| | Perfluoro silane | Trichloro(1H,1H,2H,2H PerfluoroOctyl)Silane | $NH_2$ silane | Aminopropyl Triethoxysilane (APTES) |

VARIABLES:

- THIOLS/SILANES CONCENTRATION
- SPEED OF WITHDRAWAL/DIPPING

# CARATTERIZZAZIONE

CONTACT ANGLE MEASUREMENTS (WATER) Au SUBSTRATE/THIOLS




**Item 1:**
**$[CH_3]$ = $10^{-3}$ mM;**
**[OH] = $10^{-2}$ mM;**
**speed = 20 μm/s**

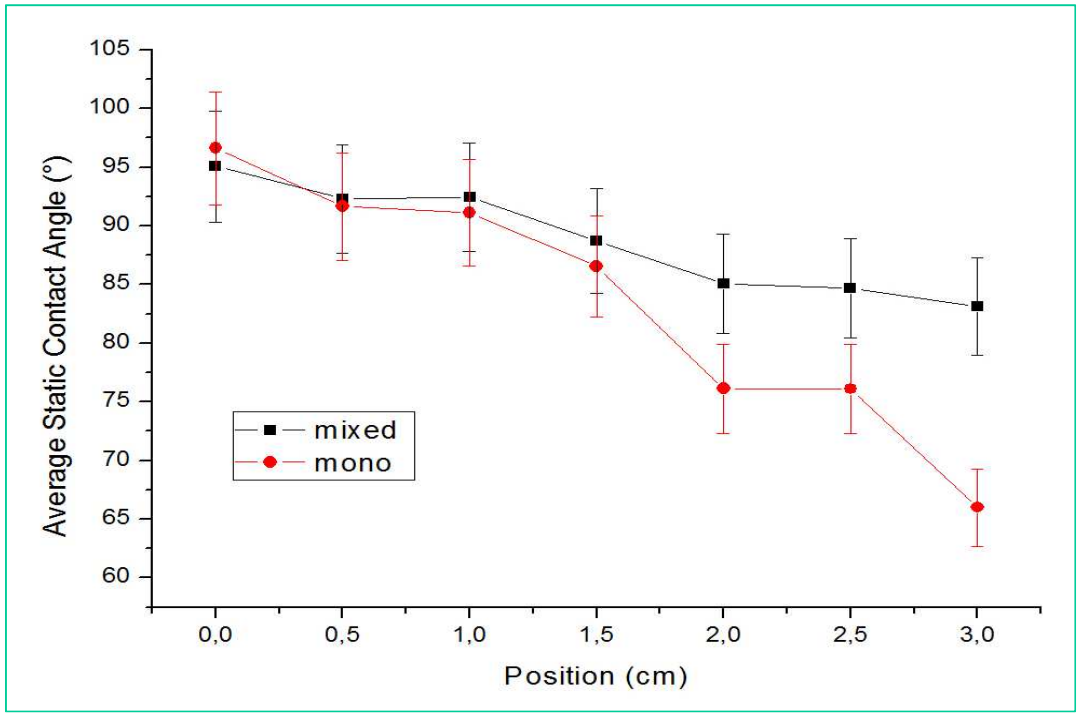
**Item 2:**
**$[CH_3]$ = 1 mM;**
**[OH] = $10^{-2}$ mM;**
**speed = 40 μm/s**

# RELATED OBSERVATIONS

- FULL COVERAGE OF MIXED THIOLS ON AU
- INFLUENCE OF ADSORBATE 1 CONCENTRATION ($CH_3$)
- LITTLE INFLUENCE OF ADSORBATE 2
- INFLUENCE OF LINEAR MOTOR SPEED (PARTIAL MONOLAYER)
- NOT MARKED WETTABILITY GRADIENT (NO DROPLETS MOVEMENT)
- NOT FLAT SURFACE (AU DEPOSITED ON GLASS)
- PRELIMINARY RESULTS (REPRODUCIBLE)

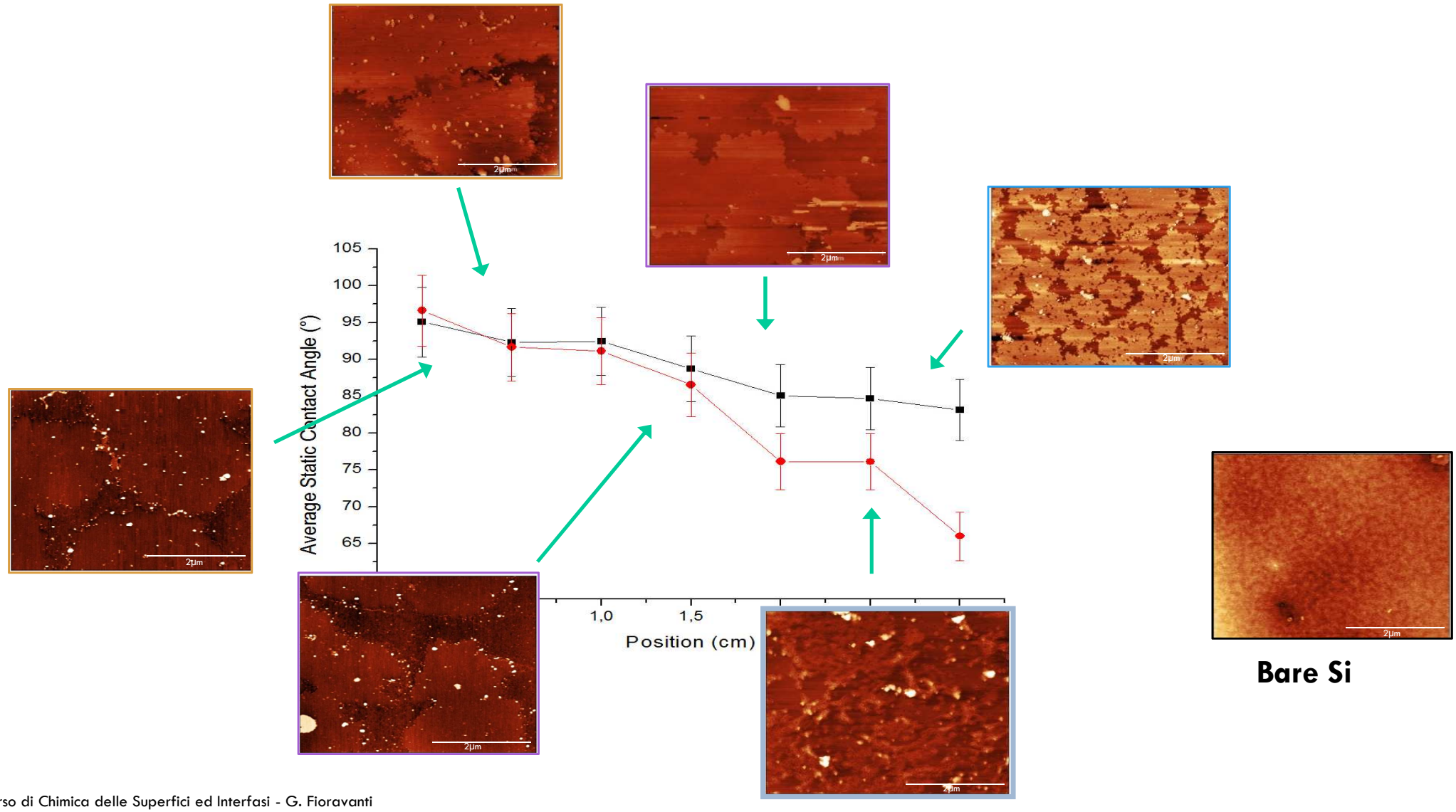
# SILANES ON SI SURFACES

CONTACT ANGLE MEASUREMENTS (WATER) - Si SUBSTRATE/SILANES



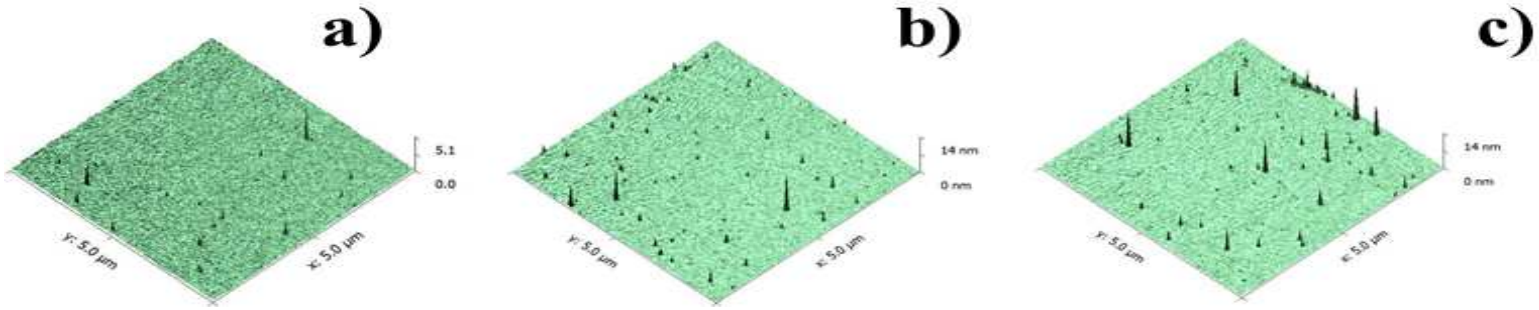

**MONO:**
PERFLUORO OCTYLSILANE

**MIXED:**
PERFLUORO OCTYLSILANE +
AMINOPROPYL TRIETHOXYSILANE


105
100
95
90
85
80
75
70
65
Average Static Contact Angle (°)
1,0
1,5
Position (cm)
2µm

**Bare Si**

# AFM CHARACTERIZATION



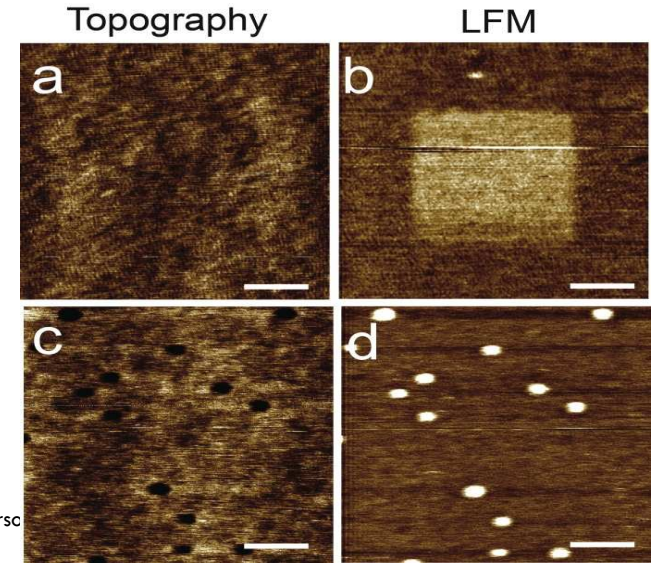

**High coverage**

c) Zone 3

b) Zone 2

a) Zone 1

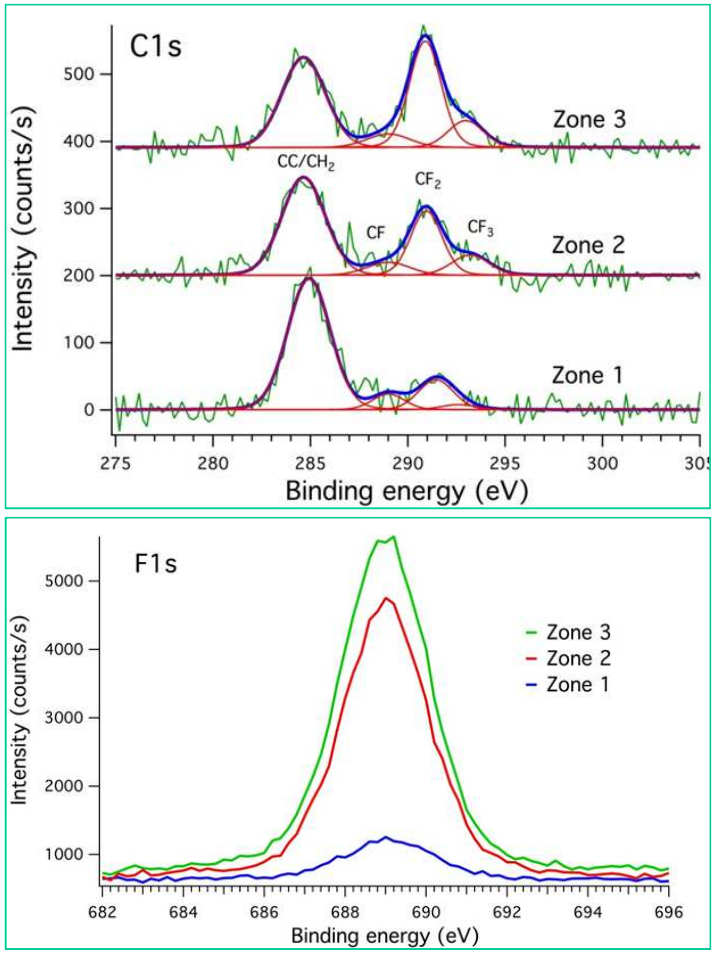
**Low coverage**




a. Typical AFM topography of zone 1 (bar 1.5 µm z scale 1 nm)
b. Corresponding LFM image recorded with 1 nN load force after nanorubbing using 4 nN loading force in the central zone.
c. Typical AFM topography of zone 3 (bar 1.5 µm z scale 1.5 nm)
d. Corresponding LFM image of c.

# XPS CHARACTERIZATION

XPS characterization: C1s and F1s evolution in the three regions of the wettability gradient.



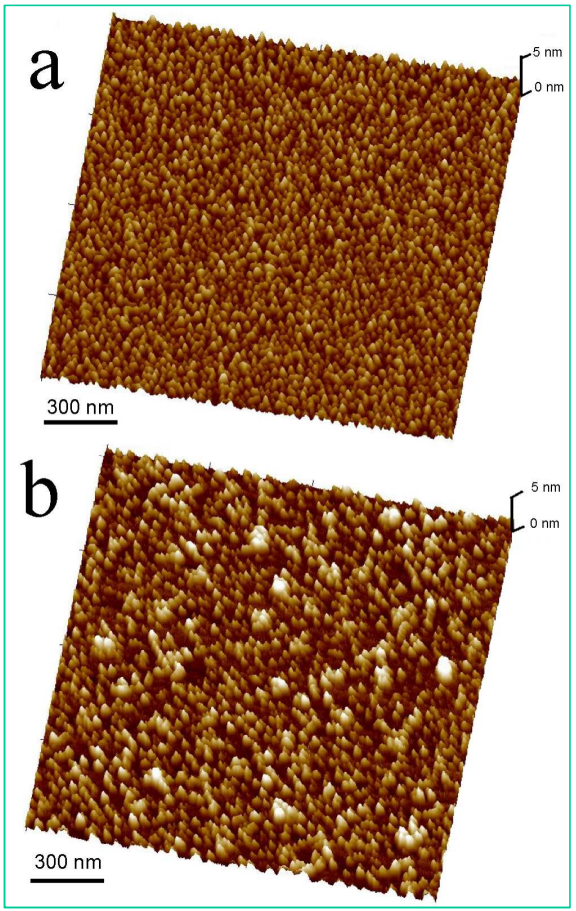


High coverage

Low coverage

# AFM CHARACTERIZATION

Typical AFM images of silicon surface functionalized by TPOS corresponding to a a) zone 1 and b) zone 3 of the samples.

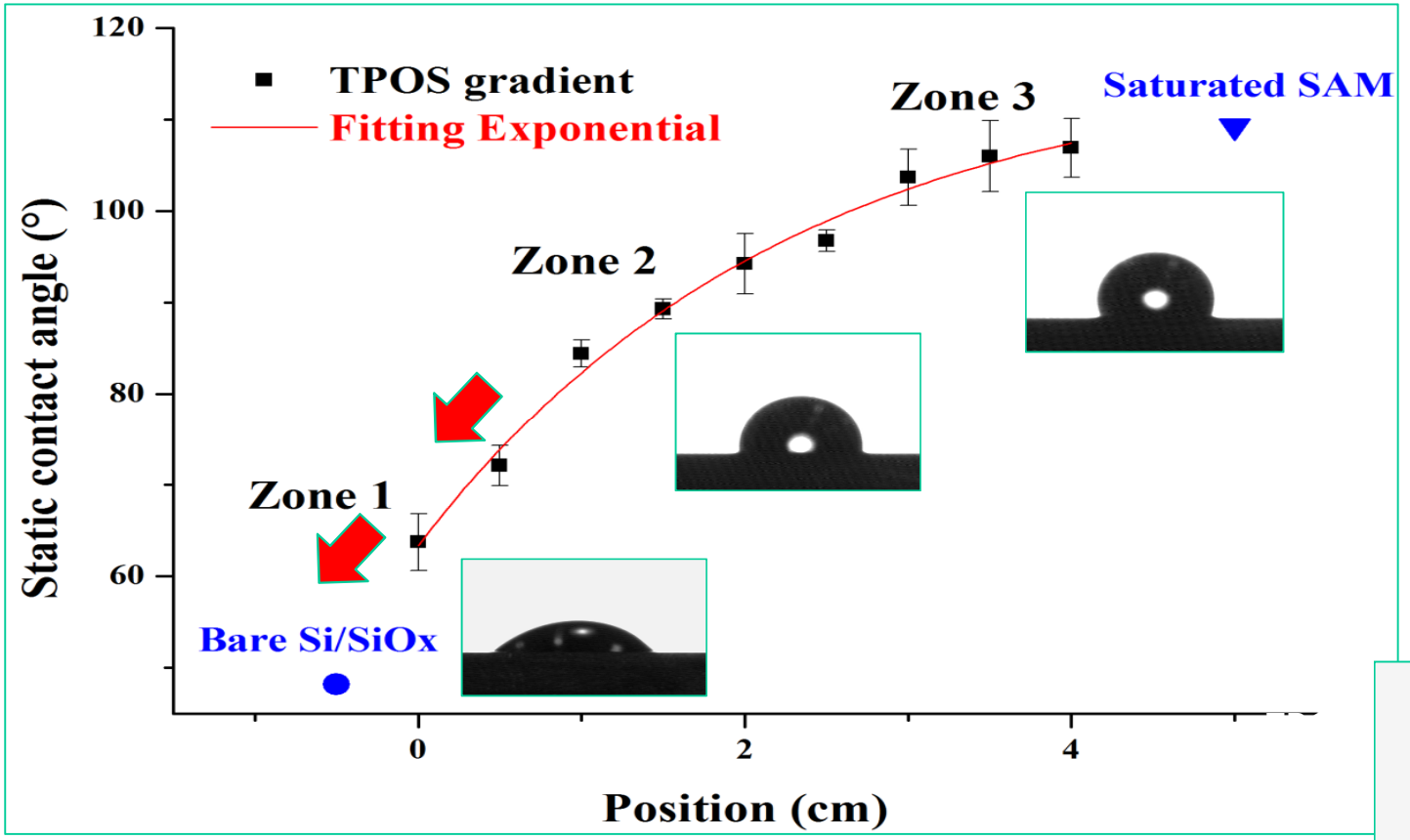




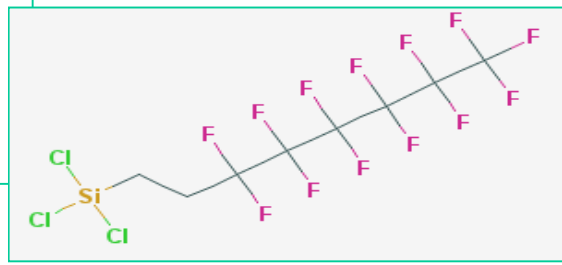
High coverage

Low coverage

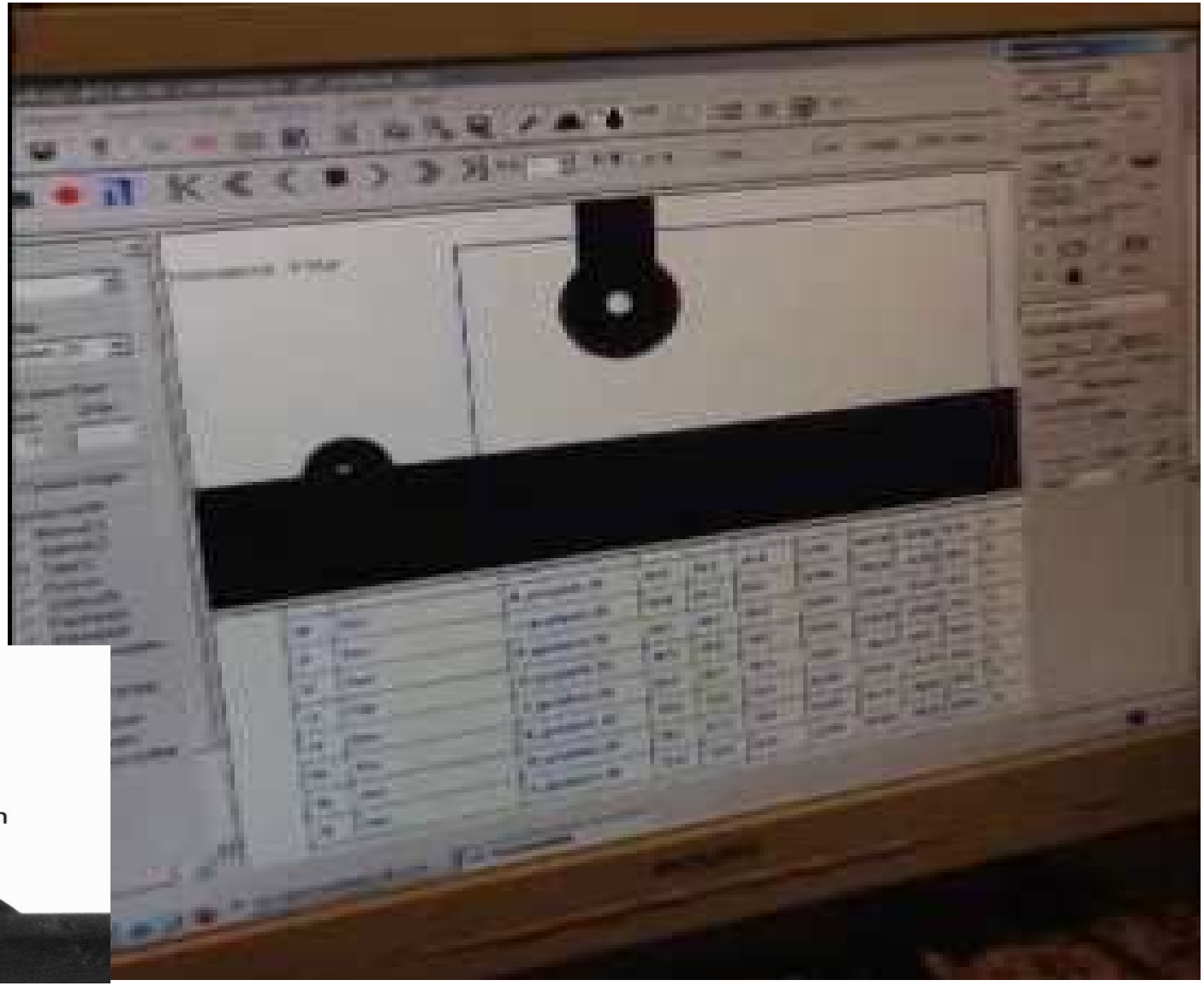
# SILANES ON SI SURFACES

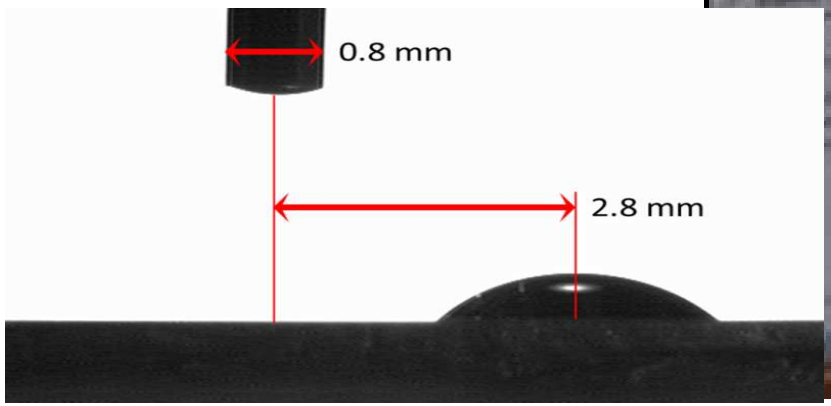



Static Water Contact Angle measurements along the gradient and exponential fit. Measurements at 25 °C in air.

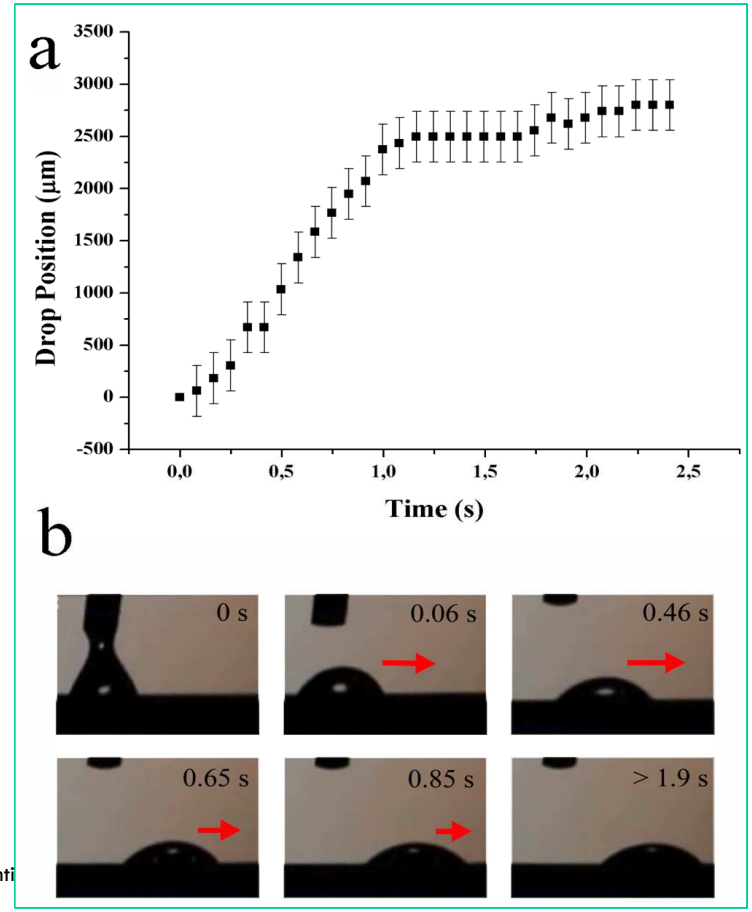


# DROPLET MOVEMENT





# DROPLET MOVEMENT



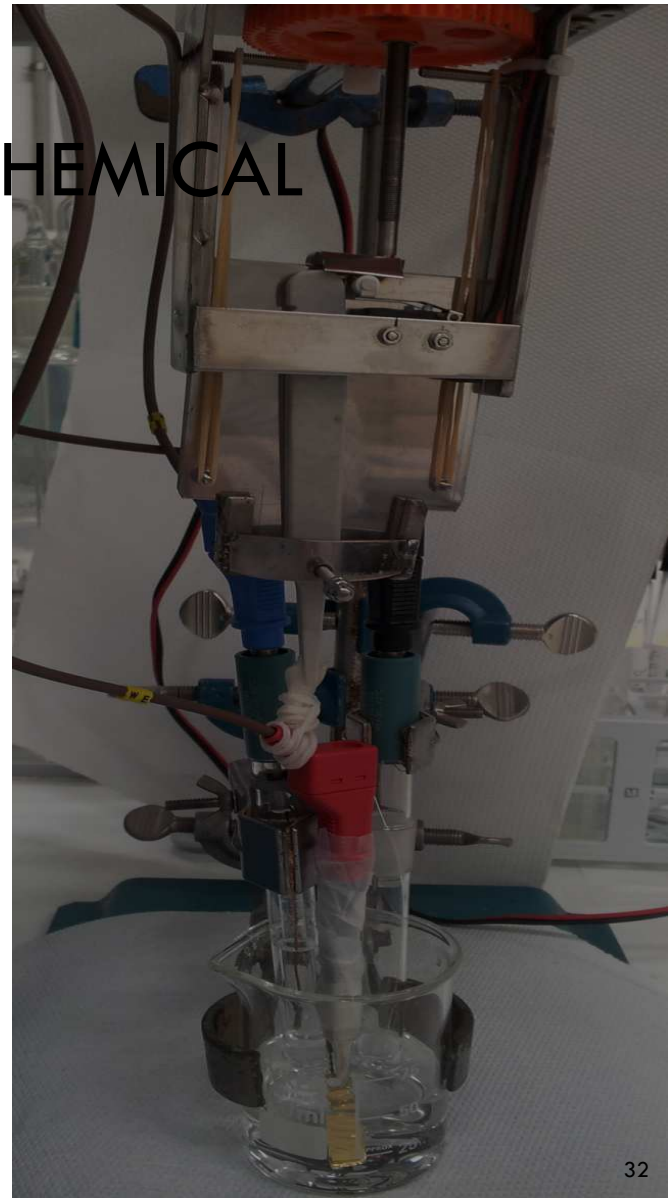

a) Plot of the droplet position of the drop during the movement along the gradient.
b) Images of the droplet in motion. The red arrows are proportional to the velocity of the movement.

# RELATED OBSERVATIONS

- MARKED SLOPE IN WETTABILITY GRADIENT (105-60°)
- DROPLETS MOVEMENT ($\Delta\theta/\Delta x > 10°$)!!!
- SILANES COVERAGE CONFIRMED BY XPS ANALYSIS
- FLAT SURFACE USEFUL FOR LATERAL FORCE AFM (?)
- PROBLEMS IN REPRODUCIBILITY (?)
- PROBLEMS IN DYNAMIC CONTACT ANGLE MEASUREMENTS

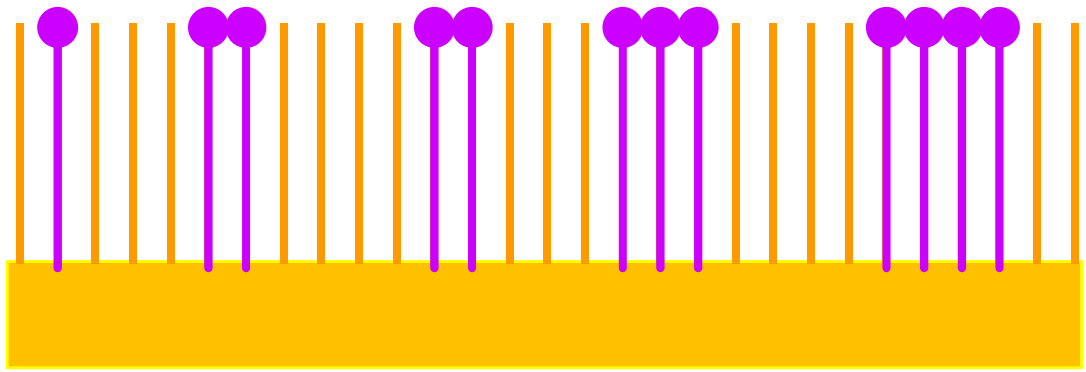
# WECD - WITHDRAWAL ELECTROCHEMICAL DESORPTION

- NEW TECHNIQUE
- DESORPTION WHILE WITHDRAWING THE SUBSTRATE
- APPLICABLE TO ANY METALLIC SURFACES COVERED BY THE PROPER ADSORBATE
- EASY AND REPRODUCIBLE

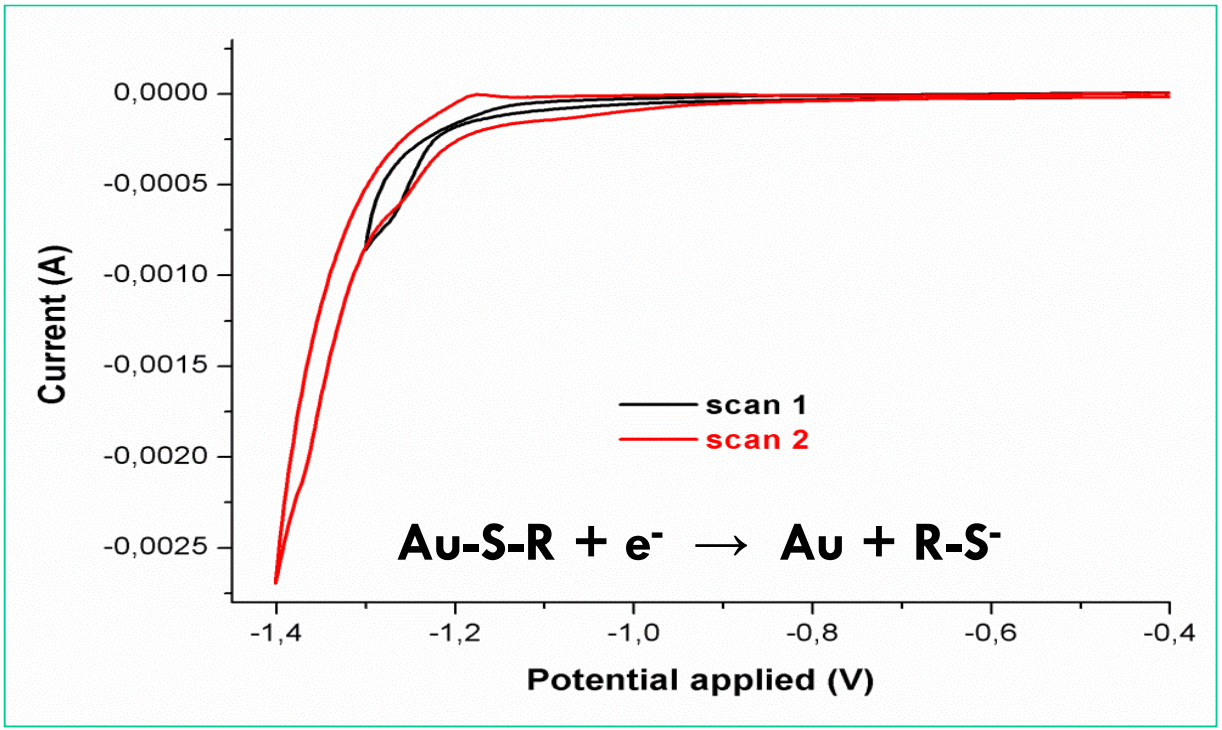


# WECD - WITHDRAWAL ELECTROCHEMICAL DESORPTION

- FIRST STEP: FULL COVERAGE OF THIOLS ($CH_3$) ON AU
- SECOND STEP: CONTROLLED ELECTROCHEMICAL DESORPTION (PARTIAL COVERAGE)
- THIRD STEP: COMPLEMENTARY ADSORPTION (OH)



# ELECTROCHEMICAL DESORPTION




0.5 M KOH solution
in Millipore water

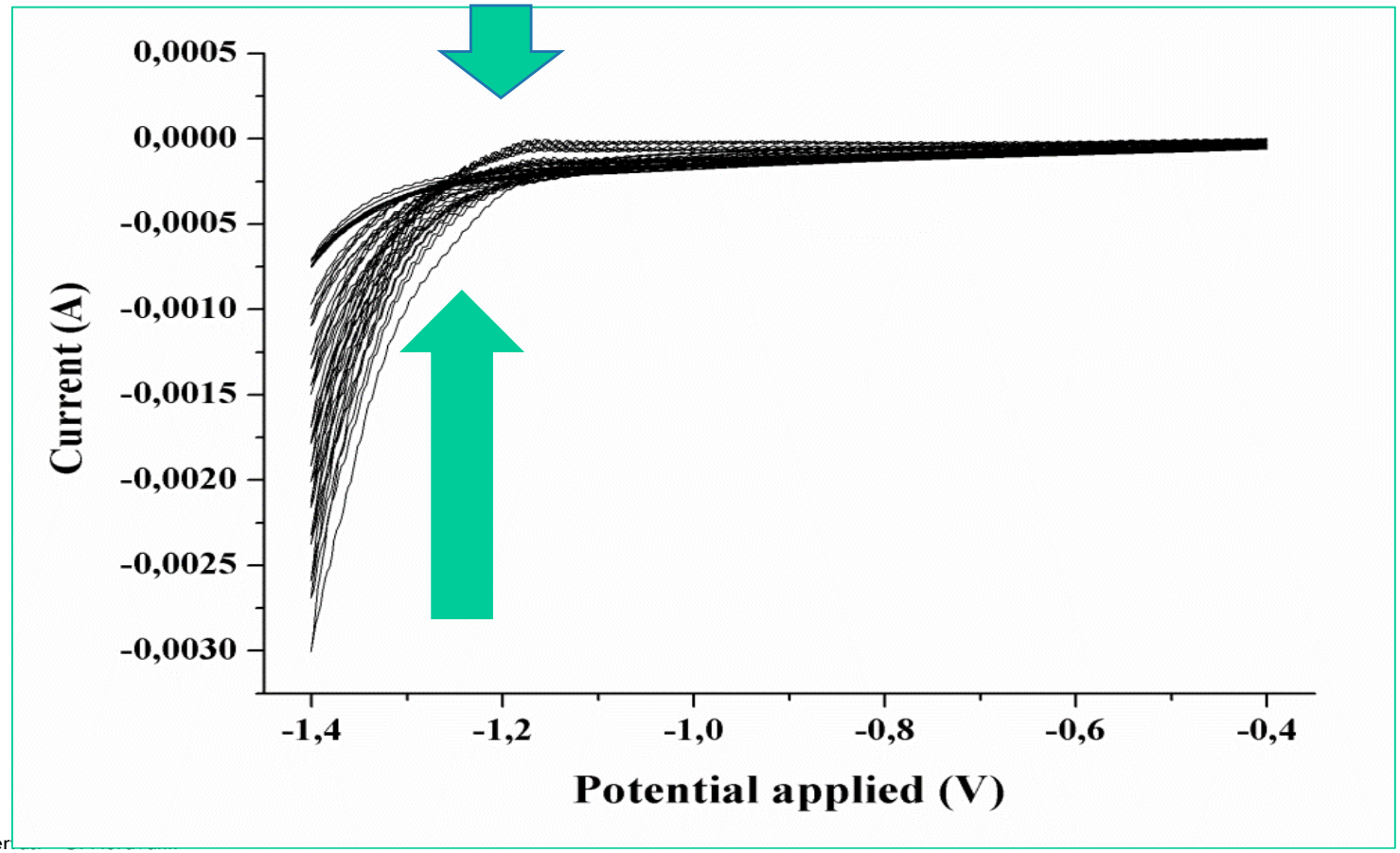
Reference: Ag/AgCl
Counter: Pt sheet

Working: SAM
covered surface

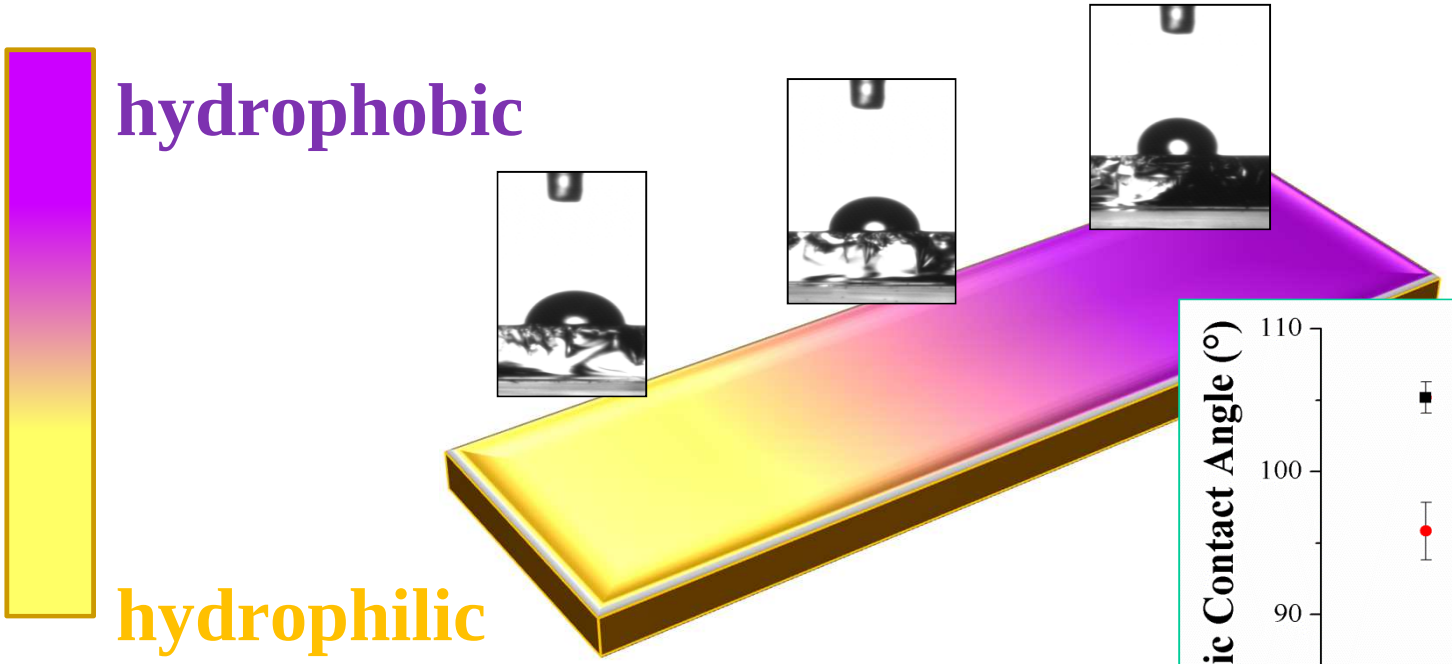
Speed: 100 mV/s

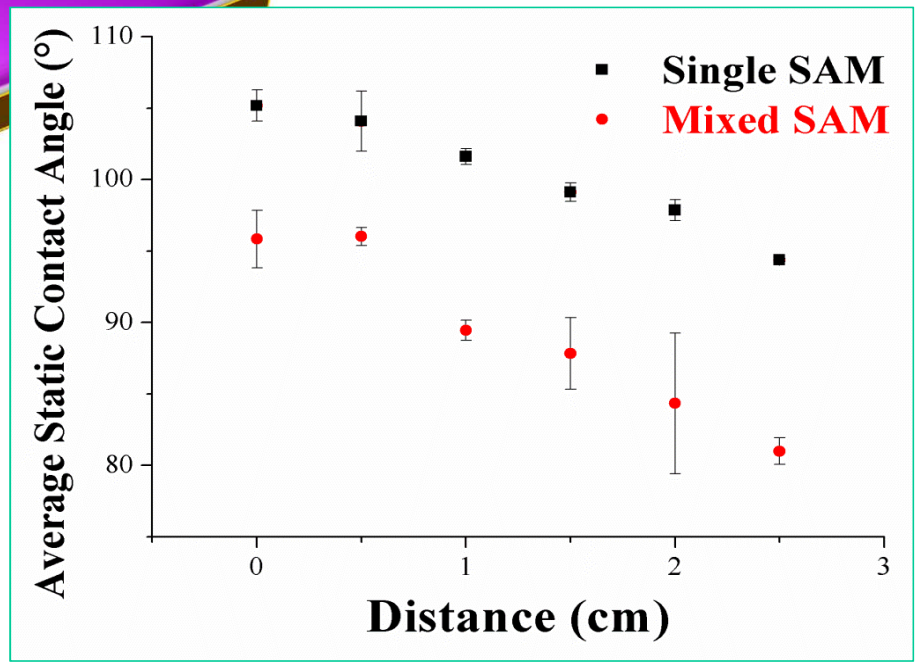
Cycling from a voltage of -0.40 V to -1.40 V, and then returning to -0.40 V.

# ELECTROCHEMICAL DESORPTION

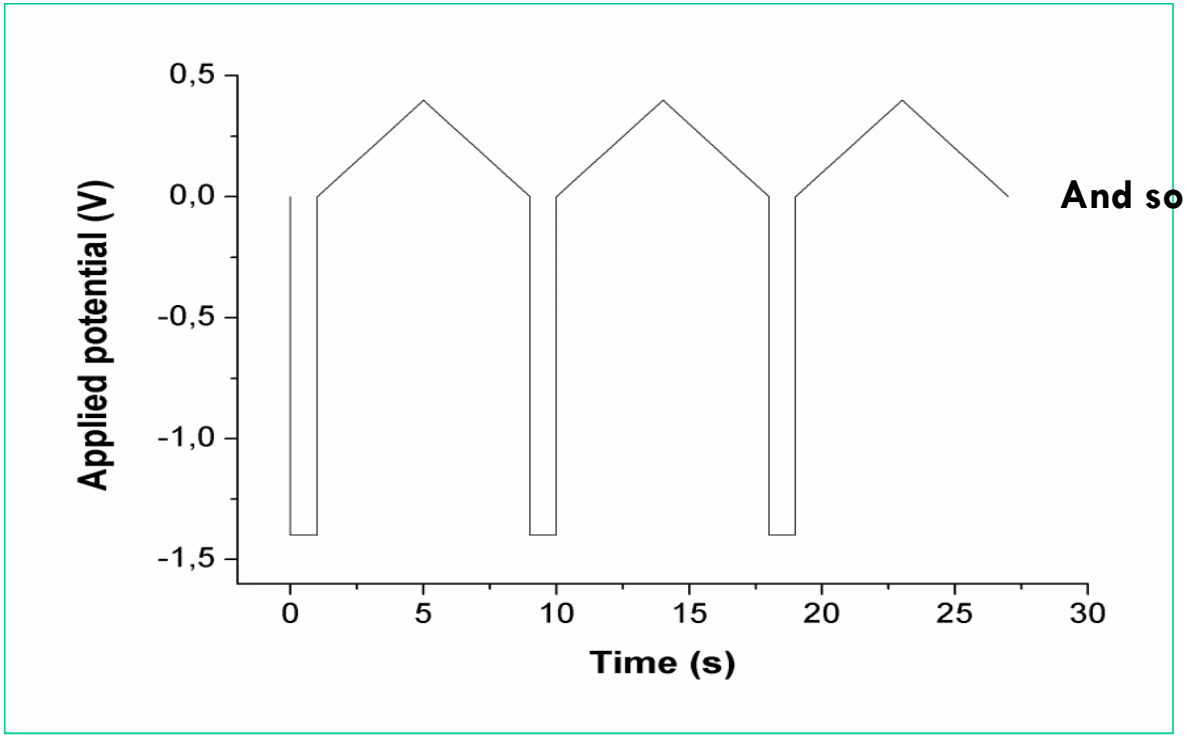


# CONTACT ANGLE MEASUREMENTS



# TIME DESORPTION



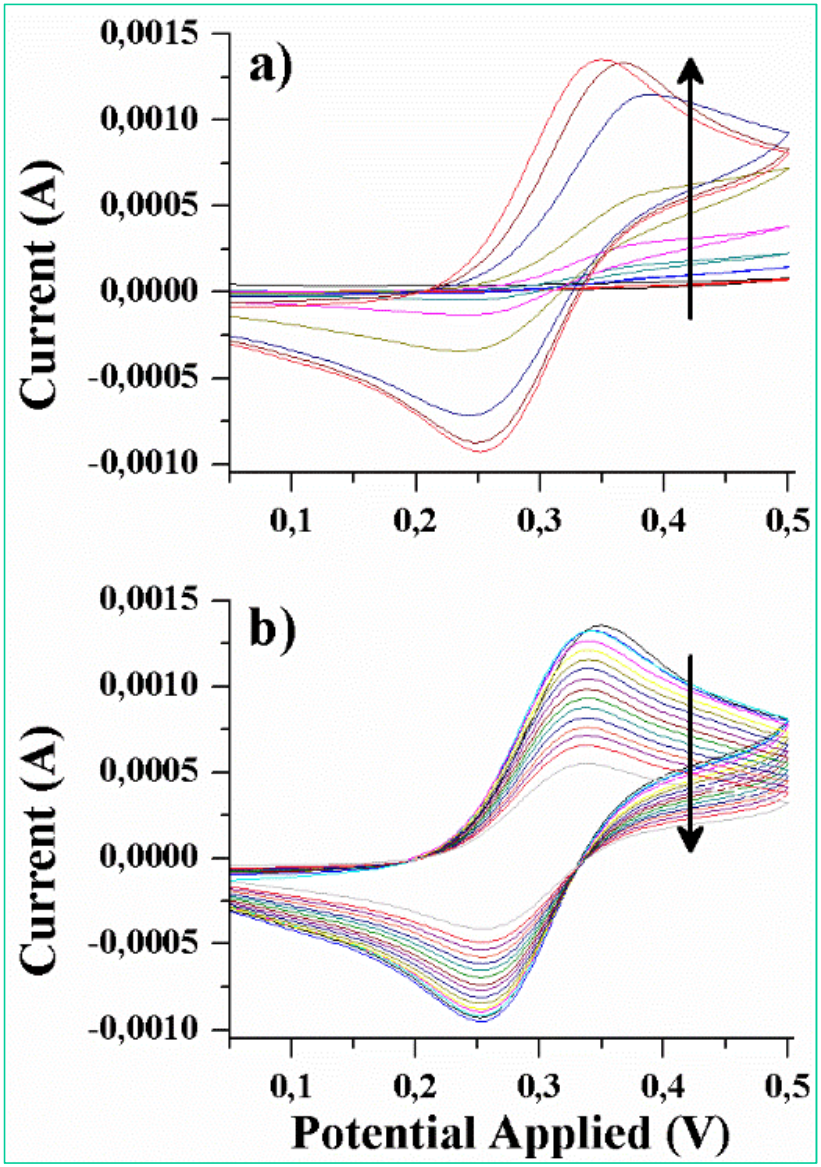

**And so on…**

Speed = 100 mV/s;
Reference electrode: Ag/AgCl;
Counter electrode: Pt wire;
Working electrode: SAM/Au.

# TIME DESORPTION - CV

Solution:
0.5 M potassium hydroxide (KOH) and
5.0 mM of ferricyanide $K_3Fe(CN)_6$

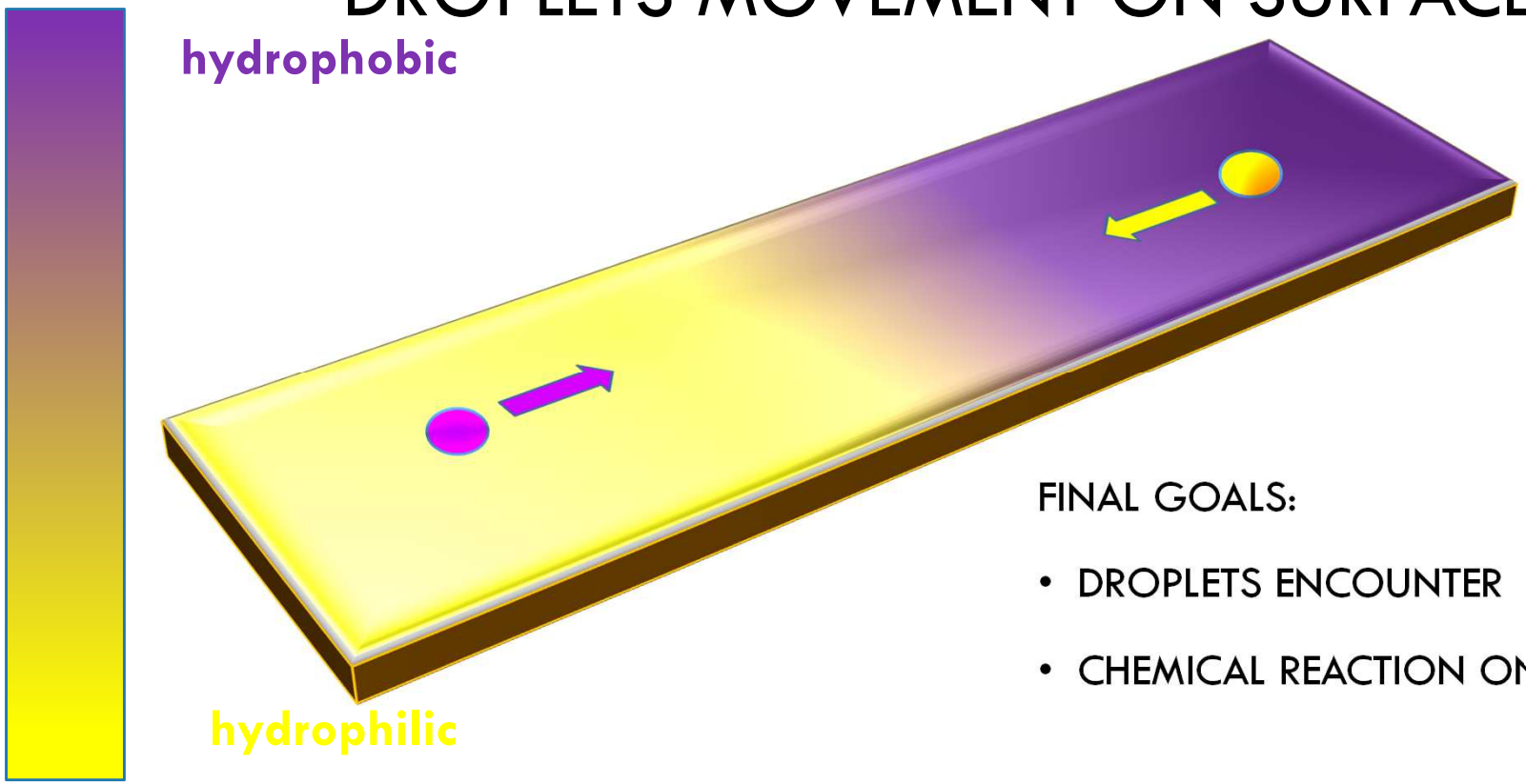
a) Repeated cyclic voltammetries from 1 to 9 cycles. b) Repeated cyclic voltammetries from cycle 10. Reference electrode: Ag/AgCl; Counter electrode: Pt wire; Working electrode: SAM/Au; 0.5 M potassium hydroxide (KOH) and 5.0 mM of potassium ferricyanide $K_3Fe(CN)_6$ solution; Speed = 100 mV/s.



# RELATED OBSERVATIONS

- FULL COVERAGE OF MIXED THIOLS ON AU
- INFLUENCE OF ADSORBATE 1 CONCENTRATION (CH3)
- LITTLE INFLUENCE OF ADSORBATE 2
- INFLUENCE OF LINEAR MOTOR SPEED (PARTIAL MONOLAYER)
- NOT MARKED WETTABILITY GRADIENT (LITTLE DROPLETS MOVEMENT)
- NOT FLAT SURFACE (AU DEPOSITED ON GLASS)
- PRELIMINARY RESULTS (REPRODUCIBLES)

# DROPLETS MOVEMENT ON SURFACE




Solvent 1

Solvent 2

FINAL GOALS:

- DROPLETS ENCOUNTER
- CHEMICAL REACTION ON SURFACE

# THE END!!!