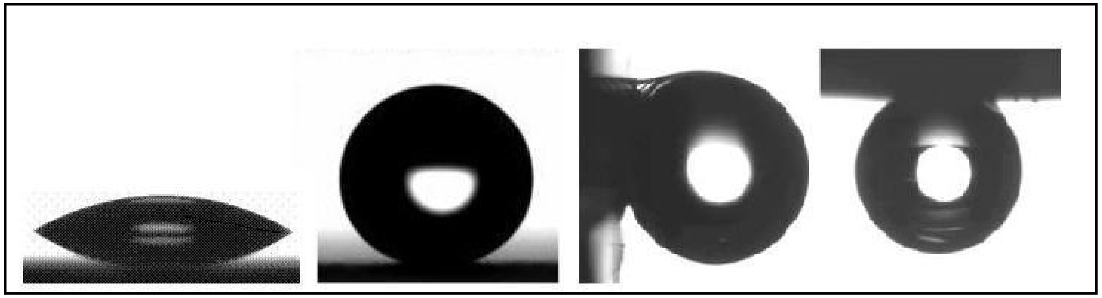
Fabrication of Superhydrophobic Cellulose Surfaces via Plasma Processing



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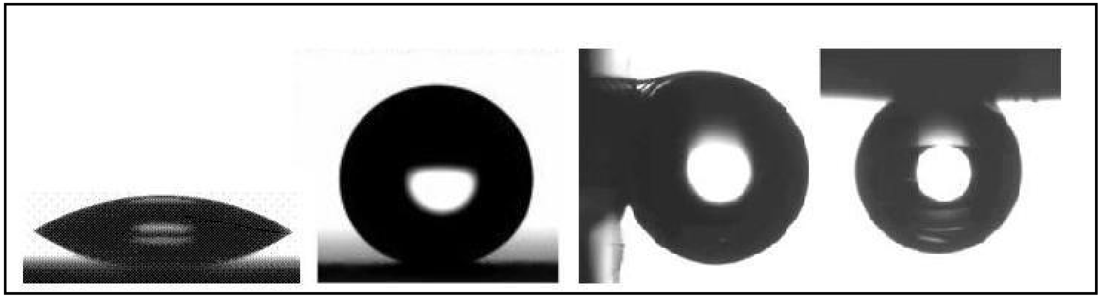
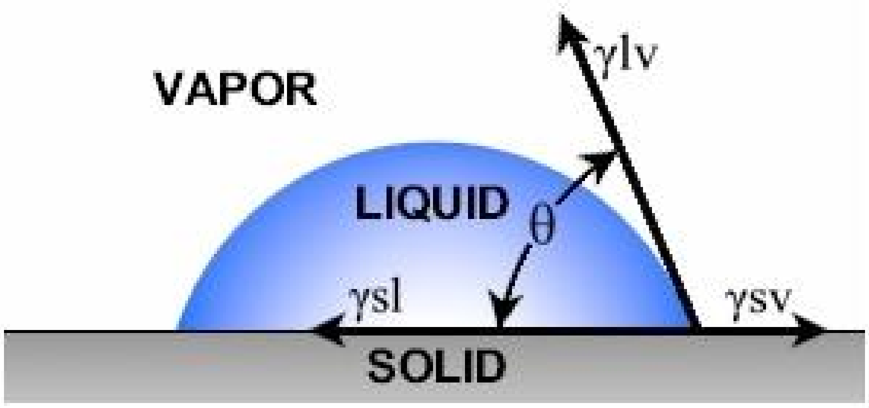
Outline

- Background
- Experimental
- Results
- Conclusions
- Acknowledgements



Definitions

- Dr. Thomas Young (1805)[1]
  - "…for each combination of a solid and a fluid, there is an appropriate angle of contact between the surfaces of the fluid, exposed to the air, and to the solid…"



Source: Rame hart Instrument Co.

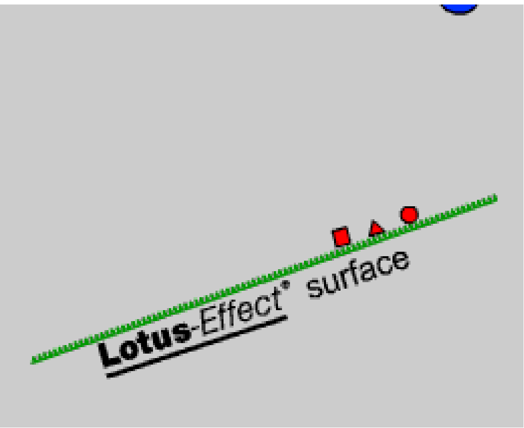
$$\gamma_{SL} + \gamma_{LV}\cos\theta = \gamma_{SV}$$

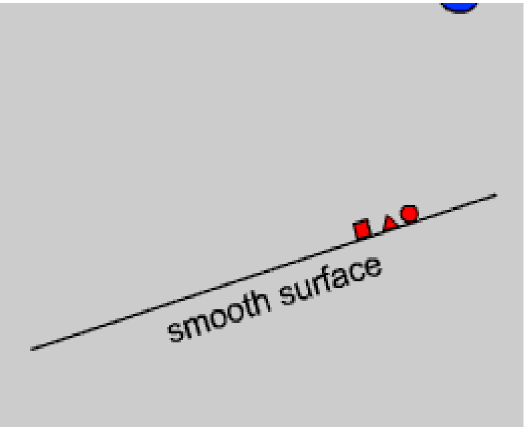
- Water Contact Angle (CA), θ < 90 → Hydrophilic
- Water Contact Angle (CA), θ > 90 → Hydrophobic
- **Water Contact Angle (CA), θ > 150 → Superhydrophobic**

1. T. Young, *Philosophical Trans. Royal Soc. London* 95, 65-87 (1805)

Superhydrophobic surfaces

- Natural superhydrophobic surfaces
  - Lotus leaves, cabbage, Indian cress
  - Butterflies, cicada wings
- Mimicking the “lotus effect”
  - Extremely water repellent surfaces (condensate water removals, transformers)
  - Self-cleaning surfaces
  - Water proof garments
  - Membranes





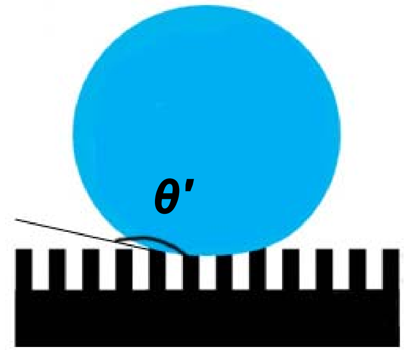
Source: Wilhelm Barthlott

How to engineer Superhydrophobicity?

- Need CA > 150
  - On smooth solid, limit is ~120 (CA for CF_3 groups)
  - Towards air, limit is ~180

$$\cos\theta' = f\cos\theta_y + (1-f)\cos 180^0$$

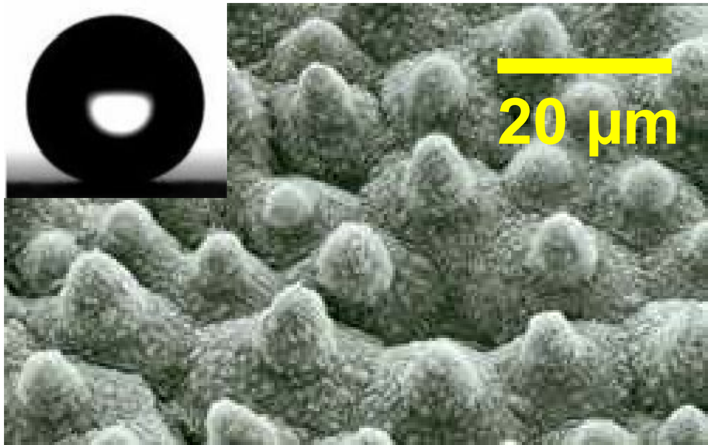
(Cassie equation)



- Rules of thumb
  - Low surface energy
  - Micron and submicron scale roughness

- Artificial superhydrophobic surfaces
  - Inorganic substrates: Si wafers, glass slides, metal sheets
    - Inflexible and not biodegradable
  - Organic: Polymers
    - Often expensive

- **Search for a biodegradable, renewable, inexpensive, biopolymer…**



Source: http://www.voyle.net/

Choice of Substrate

- Cellulose - Biodegradable, renewable, inexpensive, biopolymer!!
- Cellulose Paper

$$\cos\theta' = f\cos\theta_y + (1-f)\cos 180^0$$

  - 200 B.C to early 1800s → Hydrophilic
  - After 1800s → Hydrophobic
  - 2000s → Superhydrophobic paper [1,2]

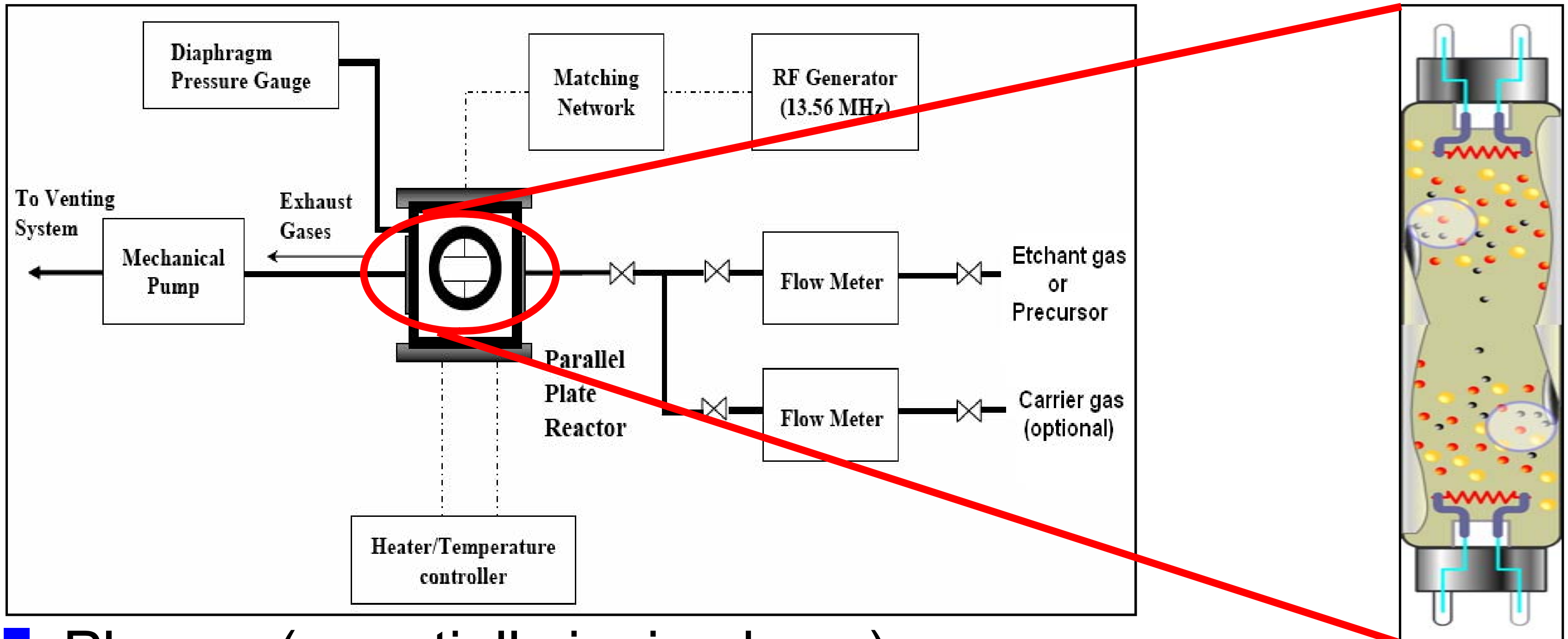
- How to obtain **"superhydrophobic paper"?**
  - Roughness
    - Selective etching -Amorphous domains and crystalline domains (nanometer length scale)
  - Low surface energy – thin film of Pentafluoroethane (PFE)
    - ~ 100 nm film covalently bonded to the top layer of fibers

1. B. Balu, V. Breedveld and D. W. Hess, *US patent (Pending)* (2007)
2. B. Balu, V. Breedveld and D. W. Hess, *Langmuir*, 24, 4785 (2008)

Experimental

Plasma Reactor
(I use This!)

Fluorescent Lamp
(We all use This!)

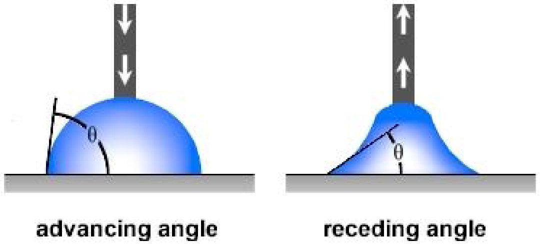


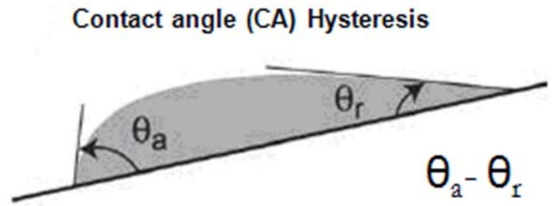
Source: www.howstuffworks.com

- Plasma (a partially ionized gas)
  - Electric current through a gas
  - Ionization, radical formation and excitation
  - Key is the type of gas used
  - Oxygen - etching
  - Pentafluoroethane - polymerization

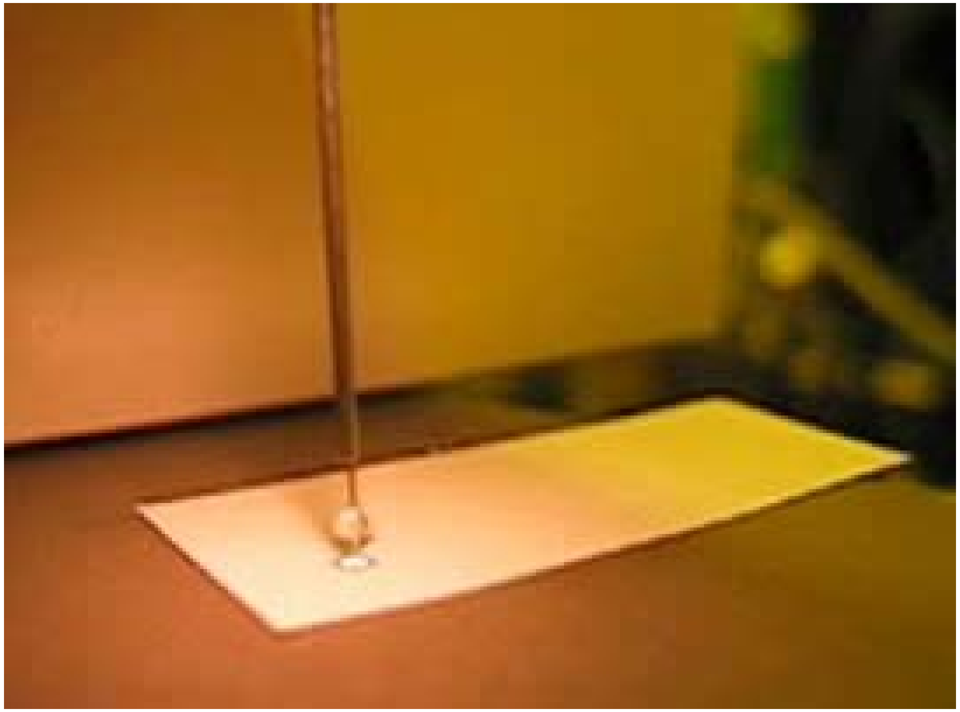
Superhydrophobic Paper

- Contact angle hysteresis





- Plasma processing
  - Etching time → 30 min
  - Deposition time → 2 min



CA $_{advancing}$	161.9 0.1
CA $_{receding}$	158.3 1.1
CA hysteresis	3.5 1.1

B. Balu, V. Breedveld and D. W. Hess, *Langmuir*, 24, 4785 (2008)

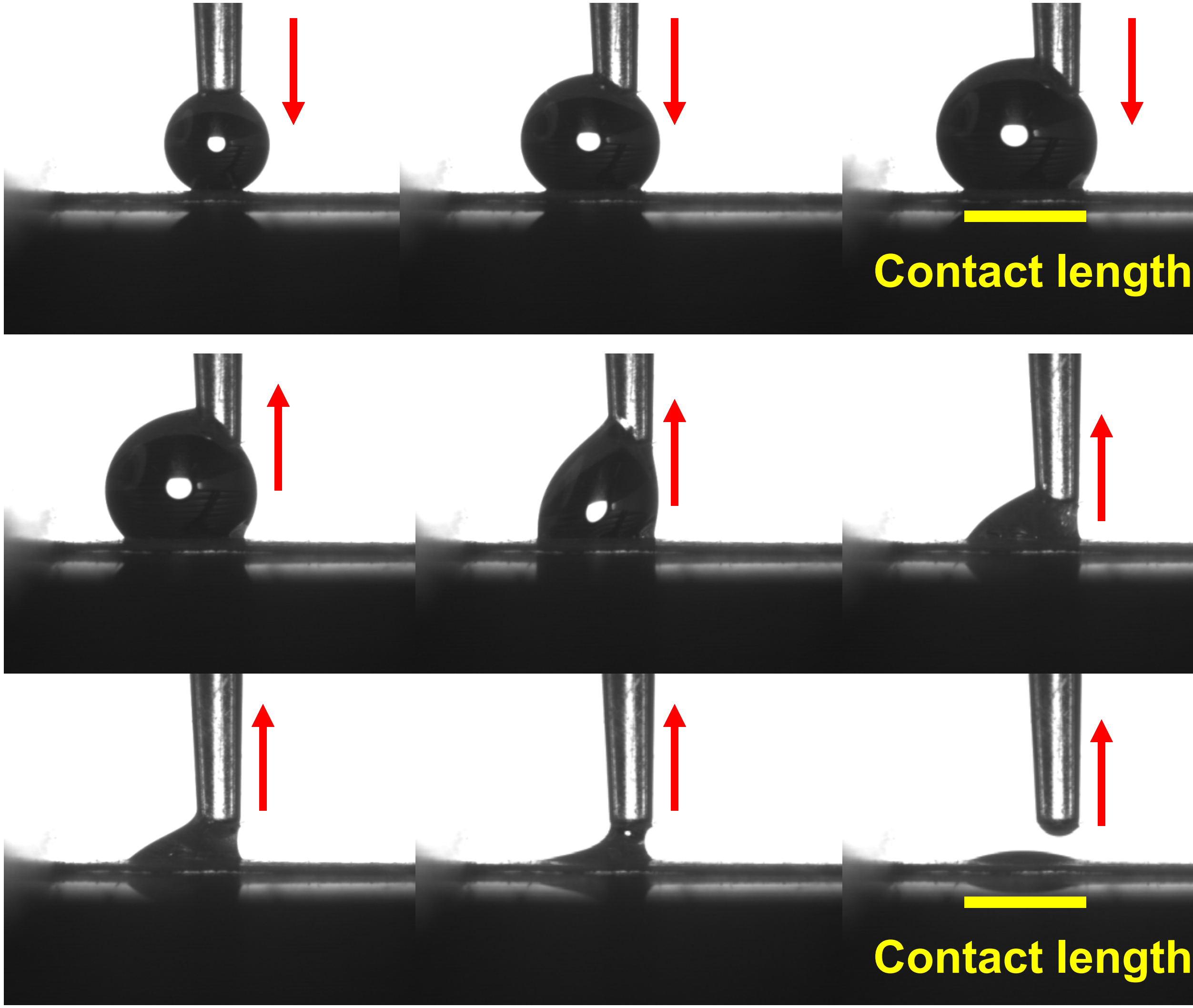
Superhydrophobic Paper

- Plasma processing
  - Etching time → 0 min
  - Deposition time → 2 min

Superhydrophobic!

CA $_{advancing}$	155.6	4.0
CA $_{receding}$	8.4	6.8
CA hysteresis	147.2	6.8

Hydrophilic!

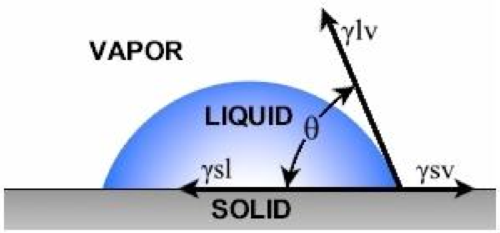


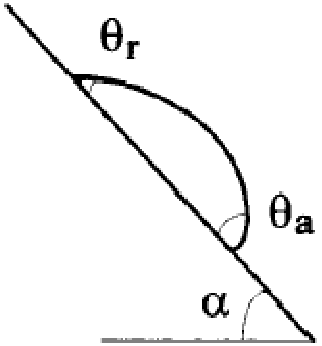
- No apparent decrease in the solid-liquid contact area
- High hysteresis for a superhydrophobic surface not reported so far!

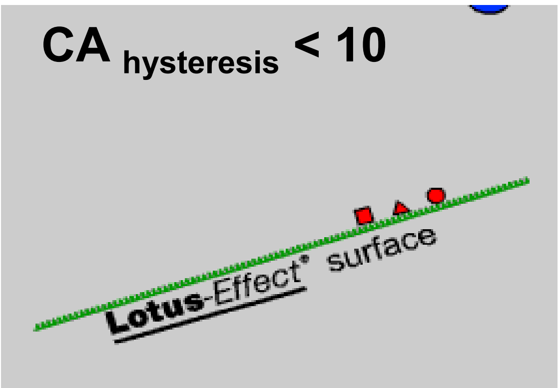
B. Balu, J. S. Kim, V. Breedveld and D. W. Hess, *J. Adhes. Sci. Technol.*, in press

Water repellency and superhydrophobicity

- Young's equation – single contact angle
- Hysteresis and adhesion force
  - Furmidge equation[1,2]
    - $mg \sin \alpha = w\, \gamma_{LV} (\cos \theta_r - \cos \theta_a)$







Contact angle	Roll-off	Sticky
CA $_{advancing}$, θ_a	161.9 0.1	155.6 4.0
CA $_{receding}$, θ_r	158.3 1.1	8.4 6.8
CA hysteresis, $\theta_a - \theta_r$	3.5 1.1	147.2 6.8

1. Furmidge, C. G., *J. Colloid Sci*., 17, 309 (1962)
2. Kawasaki, K., *J. Colloid Sci*., 15, 402 (1960)

Confusing nomenclature

CA advancing	CA hysteresis	Terms used in the literature
>150	<10	"Absolutely hydrophobic", "Water-repellant", "Ultrahydrophobic" and "Superhydrophobic"
>150	>10	"Ultra water-repellant","Super water-repellent" and "Superhydrophobic"
>150	Not reported	"Ultrahydrophobic", "Water repulsive" and "Superhydrophobic"

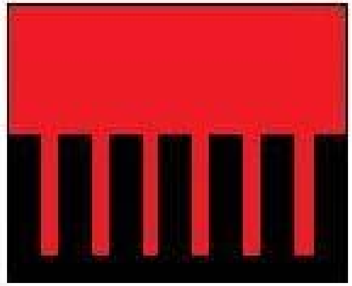
Two simple terms to categorize droplet behavior[1]

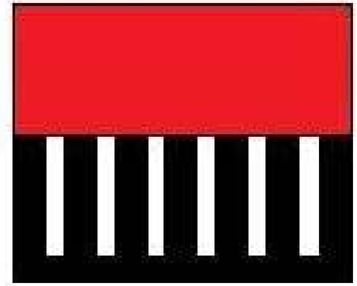
Terminology	CA $_{advancing}$, θ_a	CA hysteresis, $\theta_a - \theta_r$
"Roll-off" superhydrophobic	>150	<10
"Sticky" superhydrophobic	>150	>10

1. B. Balu, V. Breedveld and D. W. Hess, *Langmuir*, 24, 4785 (2008)

Mechanism

Ideal Wenzel state
(liquid penetrate roughness)





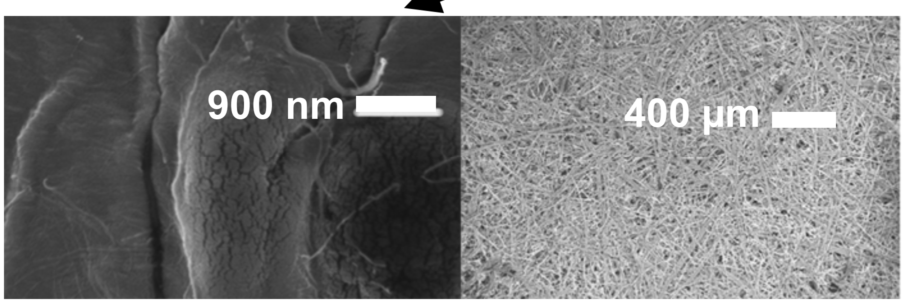
Ideal Cassie state
(liquid does not penetrate roughness)

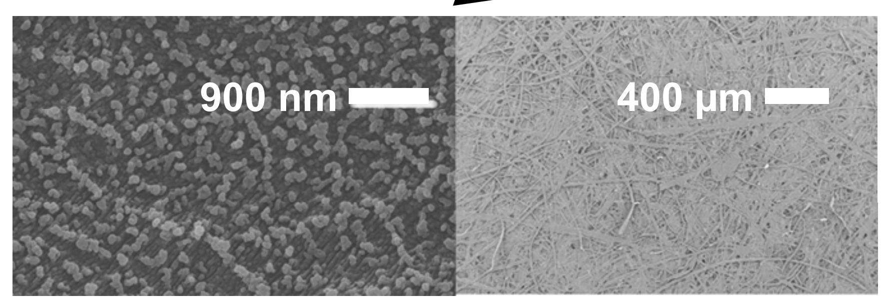
Nano-scale → Wenzel state
Micro-scale → Cassie state

Nano-scale → Cassie state
Micro-scale → Cassie state

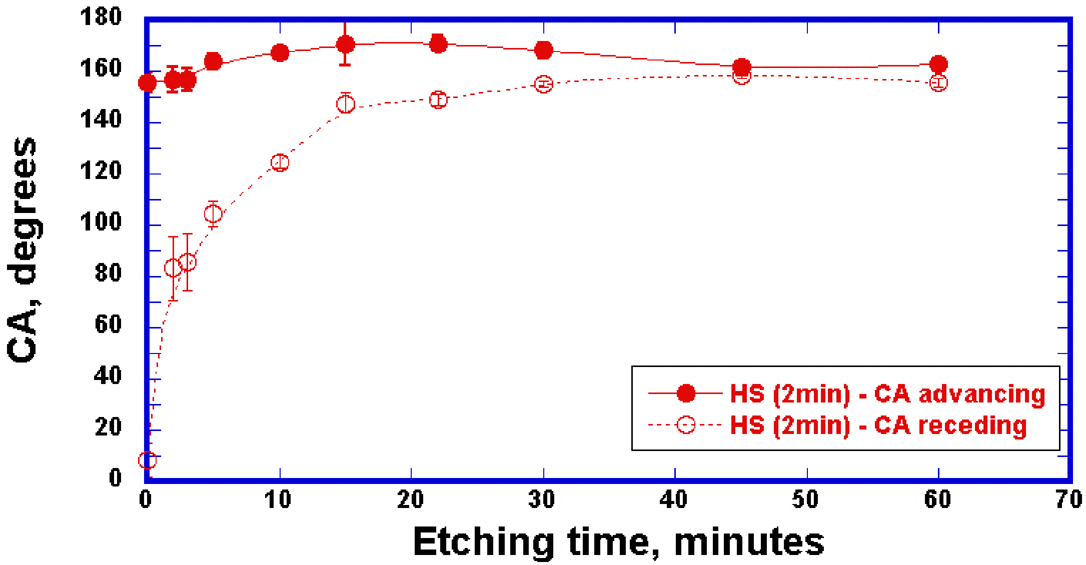
"Sticky"

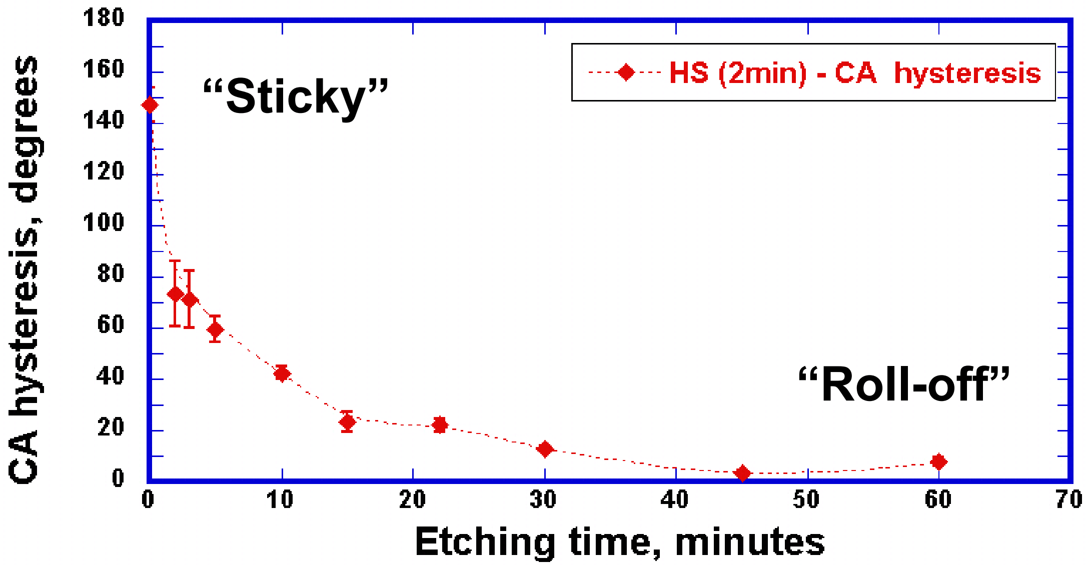
"Roll-off"





Tunability of adhesion

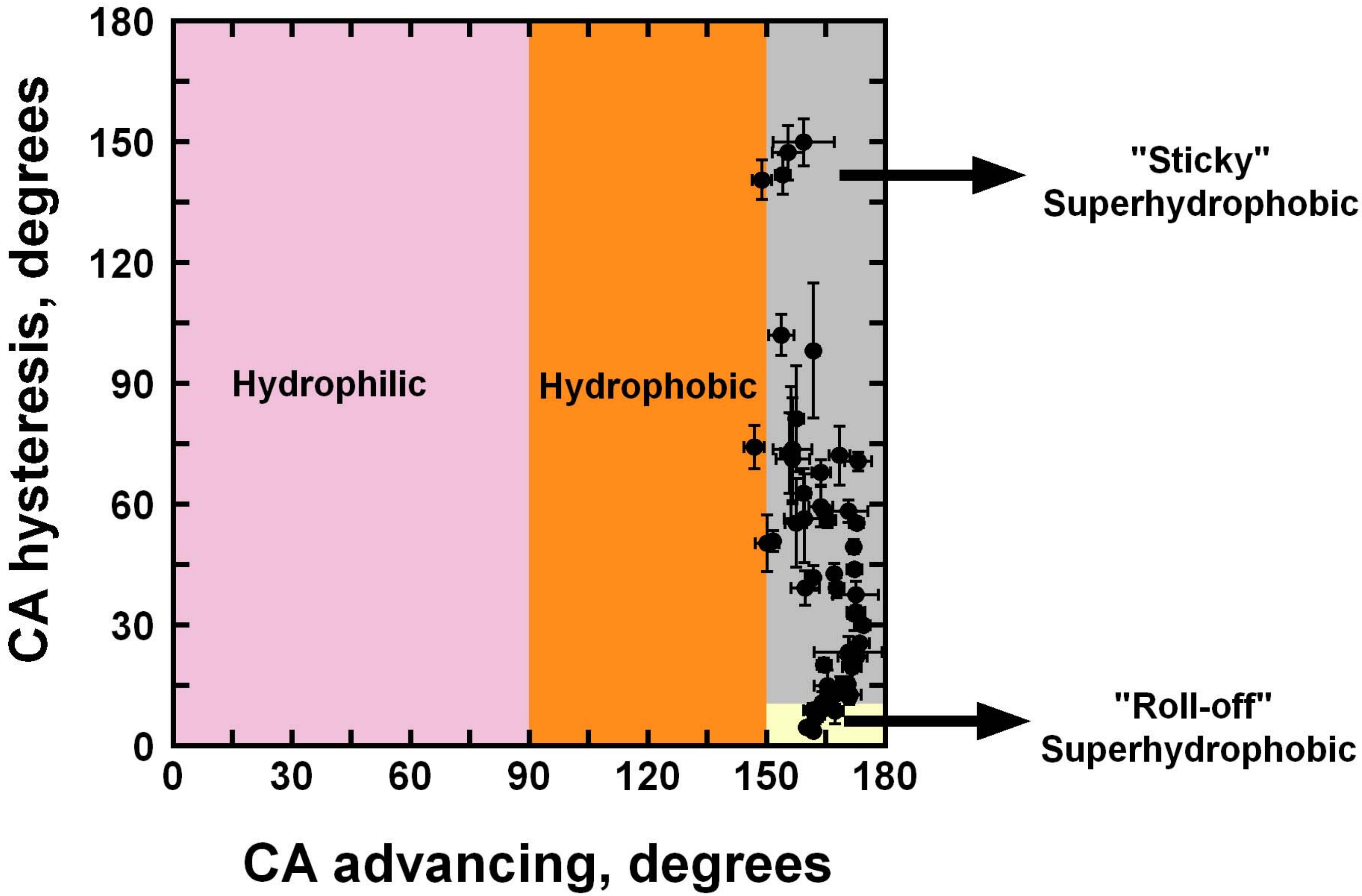




- Plasma processing
  - Etching time → variable
  - Deposition time → 2 min
- All are superhydrophobic
- Tunability of adhesion
  - Sticky to roll-off
  - CA hysteresis
    →147 to 3

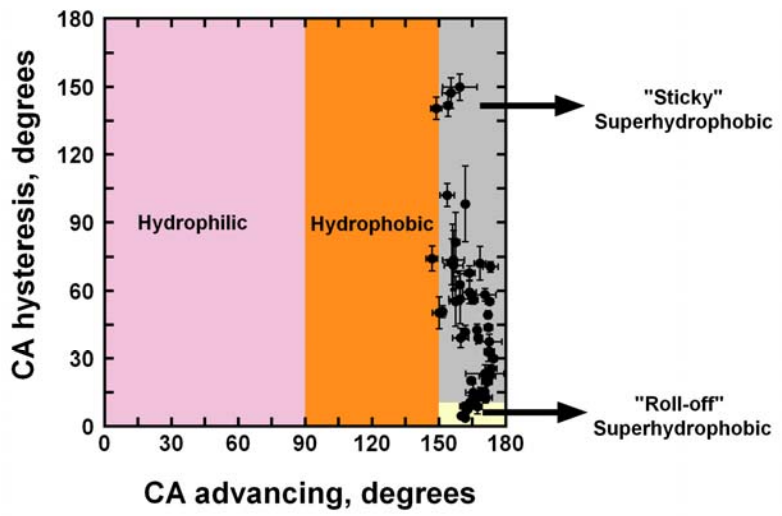
Can Independently vary CA and adhesion force!

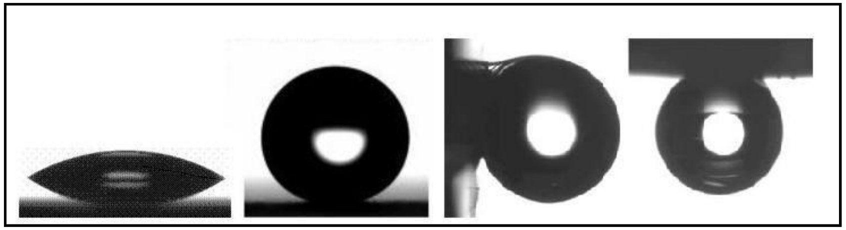
Conclusions



Conclusions (Contd…)

- Tunability of adhesion
  - "Roll-off" and "Sticky"
  - Controlled transition from "Roll-off" to "Sticky"
- Potential Applications
  - Static transfer of fluids ("tweezer" for water drops) and microfluidic devices
  - Inexpensive substrate





Acknowledgements

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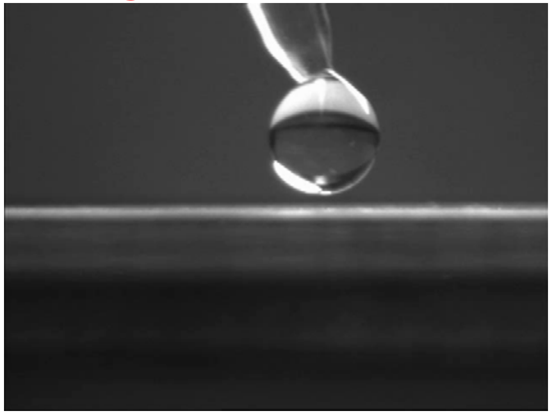
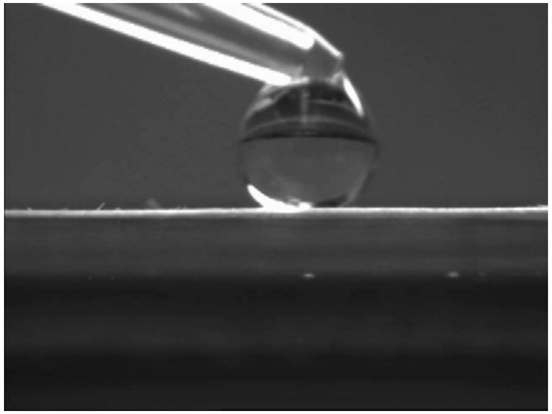
- Jong Suk Kim
- Dr. Ashwini Sinha (Praxair)
- Yonghao Xiu (Hess Research Group)
- Hess and Breedveld Research Group Members

Questions?

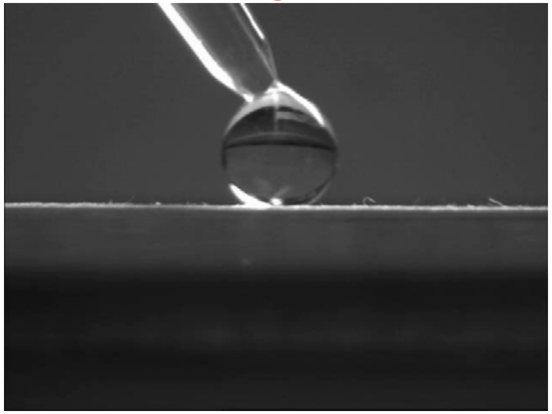
Hydrophilic



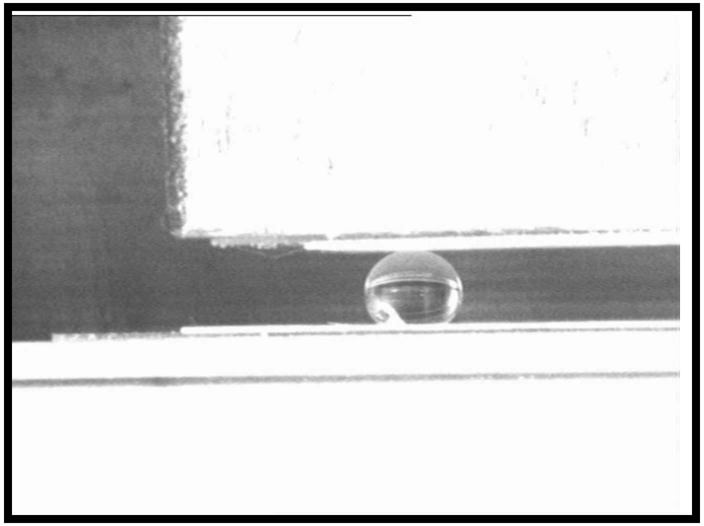
"roll-off" SH



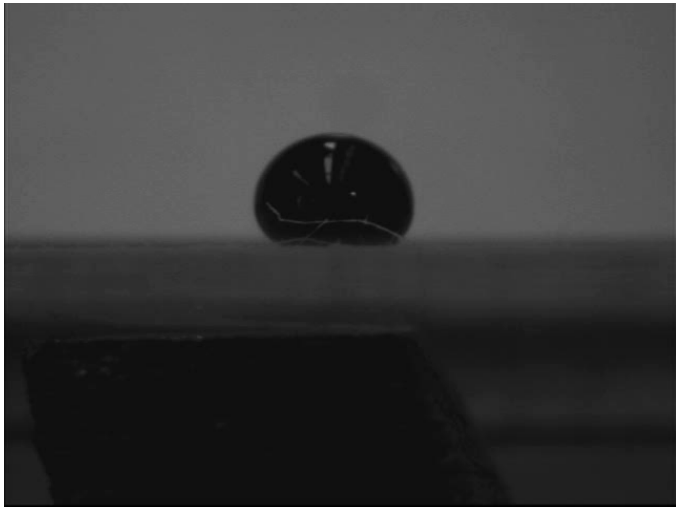
"sticky" SH



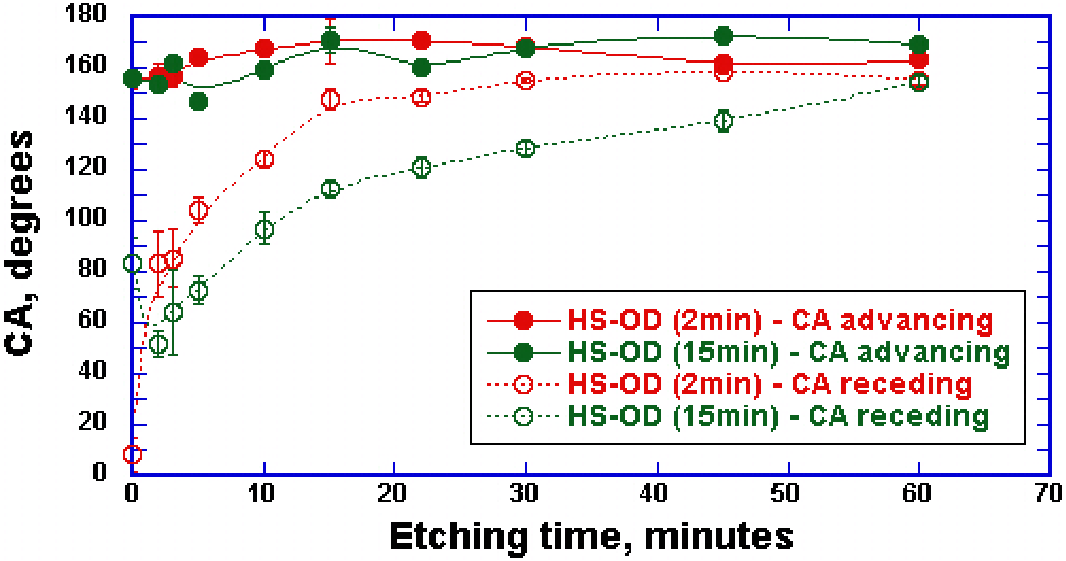
Squeezing a drop between two SH surfaces

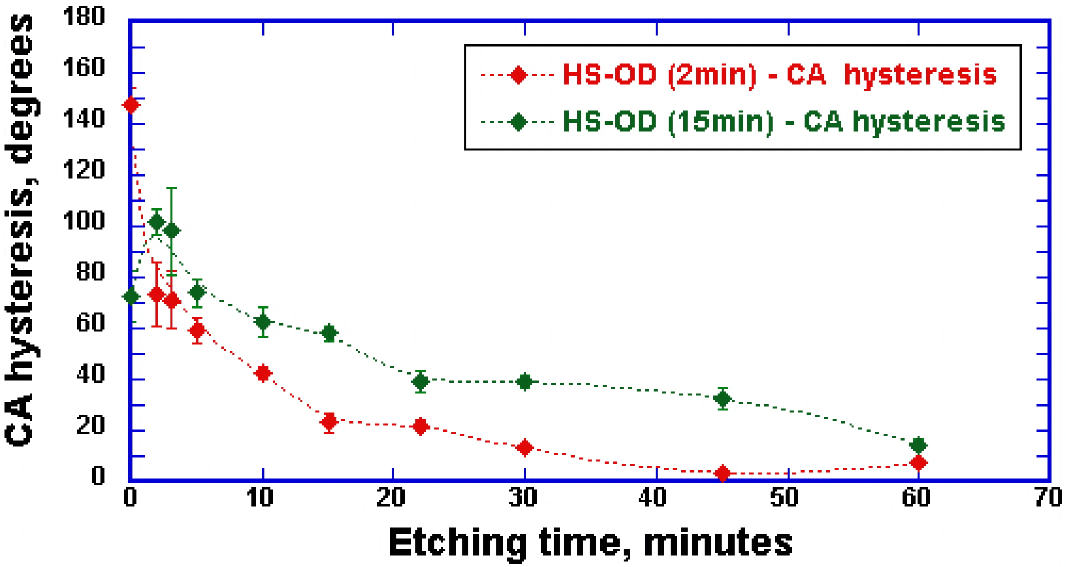


Moving a magnetic water drop on a SH surface



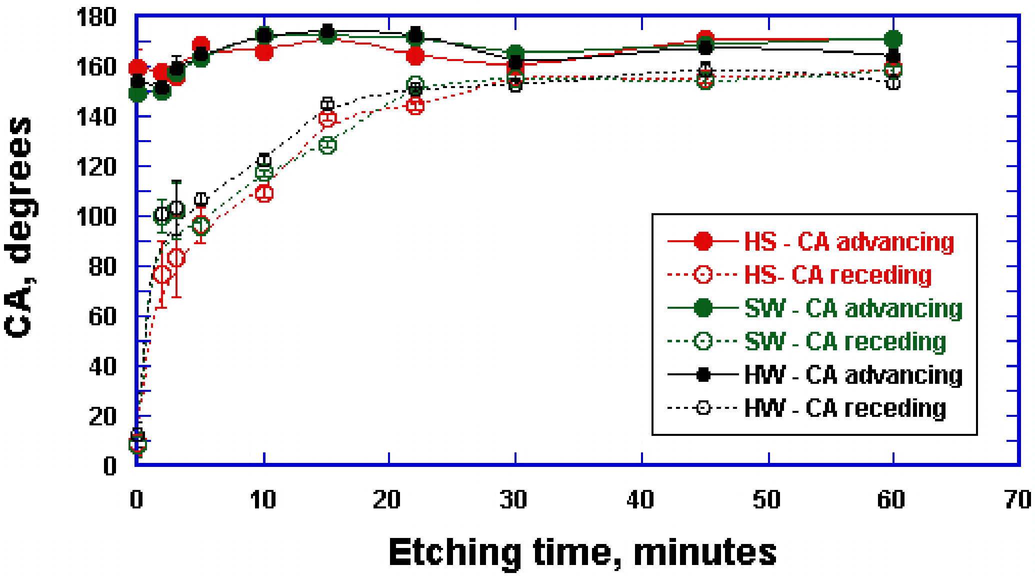
Effects of nano-scale roughness



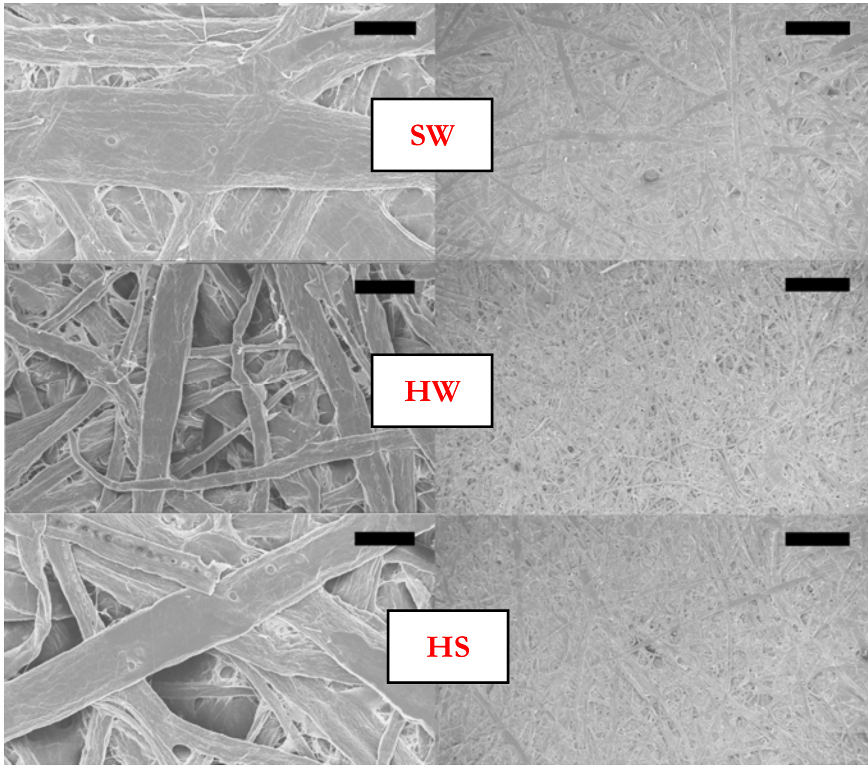


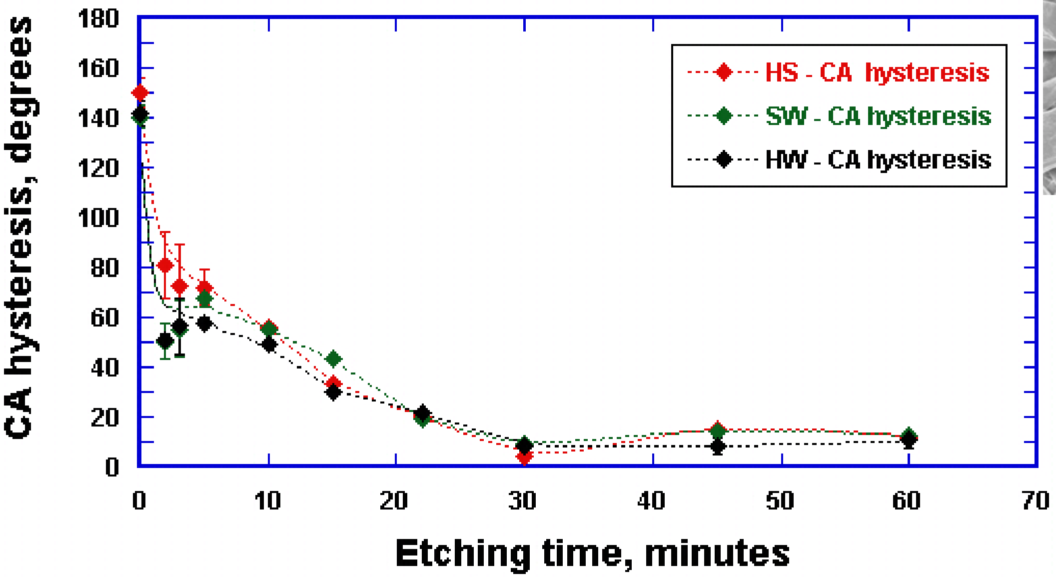
- Significant impact on the receding CA
- Enhancement of the roughness
  - Unique feature of plasma deposition
- Hysteresis
  - sensitive to nano-scale roughness
  - Not sensitive to micro-scale roughness

Effects of Fiber types



Scale ~ 40 um??





- SW – large fibers
- HW – small fibers
- No significant variation in hysteresis

Non-conformal deposition

- Non-conformal deposition