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…”

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

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

Source: Ramehart Instrument Co.
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 CF₃ 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
  - 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

\[
\cos \theta' = f \cos \theta_y + (1 - f) \cos 180^\circ
\]

Experimental

Plasma Reactor
(I use This!)

- Diaphragm Pressure Gauge
- Mechanical Pump
- Exhaust Gases
- Matching Network
- RF Generator (13.56 MHz)
- Flow Meter
- Parallel Plate Reactor
- Heater/Temperature controller
- To Venting System

Fluorescent Lamp
(We all use This!)

- Etchant gas or Precursor
- Carrier gas (optional)

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

Source: www.howstuffworks.com
Superhydrophobic Paper

- Contact angle hysteresis

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

<table>
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<th>CA\textsubscript{advancing}</th>
<th>CA\textsubscript{receding}</th>
<th>CA hysteresis</th>
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<td>161.9 0.1</td>
<td>158.3 1.1</td>
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Superhydrophobic Paper

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

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<th>CA (_{\text{advancing}})</th>
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<tr>
<td>CA hysteresis</td>
<td>147.2</td>
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- No apparent decrease in the solid-liquid contact area
- High hysteresis for a superhydrophobic surface not reported so far!

Water repellency and superhydrophobicity

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

<table>
<thead>
<tr>
<th>Contact angle</th>
<th>Roll-off</th>
<th>Sticky</th>
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<tr>
<td>$\theta_a$</td>
<td>161.9</td>
<td>155.6</td>
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<tr>
<td>$\theta_r$</td>
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</tr>
<tr>
<td>$\theta_a - \theta_r$</td>
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<td>147.2</td>
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Confusing nomenclature

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<th>CA advancing</th>
<th>CA hysteresis</th>
<th>Terms used in the literature</th>
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<td>&lt;10</td>
<td>“Absolutely hydrophobic”, “Water-repellant”, “Ultra hydrophobic” and “Superhydrophobic”</td>
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<tr>
<td>&gt;150</td>
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<tr>
<td>&gt;150</td>
<td>Not reported</td>
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Two simple terms to categorize droplet behavior:

<table>
<thead>
<tr>
<th>Terminology</th>
<th>CA advancing, $\theta_a$</th>
<th>CA hysteresis, $\theta_a - \theta_r$</th>
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<tr>
<td>“Roll-off” superhydrophobic</td>
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</tr>
<tr>
<td>“Sticky” superhydrophobic</td>
<td>&gt;150</td>
<td>&gt;10</td>
</tr>
</tbody>
</table>

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”

900 nm  400 µm

900 nm  400 µm
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
- IPST Fellowship
- 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

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

Scale ~ 40 um??

Etching time, minutes

CA, degrees

CA hysteresis, degrees

Etching time, minutes
Non-conformal deposition

- Non-conformal deposition