Bioinspired Nanoengineering of Multifunctional Superhydrophobic Surfaces

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Abstract:
Nature, such as plants, insects, and marine animals, uses micro/nano-textured surfaces in their components (e.g., leaves, wings, eyes, legs, and skins) for multiple purposes, such as water-repellency, anti-adhesiveness, and self-cleanness. Such multifunctional surface properties are attributed to three-dimensional surface structures with modulated surface wettability. Especially, hydrophobic surface structures create a composite interface with liquid by retaining air between the structures, minimizing the contact area with liquid. Such non-wetting surface property, so-called superhydrophobicity, can offer numerous application potentials, such as hydrodynamic drag reduction, anti-biofouling, anti-corrosion, anti-fogging, anti-frosting, and anti-icing. Over the last couple of decades, we have witnessed a significant advancement in the understanding of surface superhydrophobicity as well as the design, fabrication, and applications of superhydrophobic coatings/surfaces/materials. In this talk, the designs, fabrications, and applications of superhydrophobic surfaces for multifunctionalities will be presented, including hydrodynamic friction reduction, anti-biofouling, anti-corrosion, and anti-icing.
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The birthplace of the American Society of Mechanical Engineers (ASME)
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Outlines

• Motivation: Lesson From Nature
• Technical Backgrounds: Wetting on Rough Surfaces
• Design Issues: Why Nano?
• Nanomanufacturing Techniques for Various Substrate Materials: From Ceramic to Polymer to Metal
• Multifunctional Applications
  • Anti-Friction
  • Anti-Biofouling
  • Anti-Corrosion
  • Anti-Icing
• Concluding Remarks
Motivation

Lesson from Nature

- **Surfaces in Nature:** Three-dimensional (3D) hierarchical micro/nano-structured surfaces with tailored surface wettability and mechanical flexibility
- **Energy-Efficient & Multifunctional:** Self cleaning, Low friction, Low adhesion, Anti-fouling, Anti-reflection, Anti-frosting/icing, etc.
Nano-Engineered Superhydrophobic Surface

Potential Applications of Nanoengineered Surfaces

- Self-Cleaning
- Low Friction (Micro/Nano)
- Anti-Fouling
- Anti-Icing
- Anti-Graffiti
- Low Friction (Pipe systems)
- Anti-Microbial
- Anti-Frosting
- Anti-Fogging
- Drag Reduction (Vessels)
- Anti-Corrosion
- Anti-Snow Adhesion

And many more…
Potential Applications to Thermal/Energy Systems

Evaporative Heat Transfer

Dropwise vs. Filmwise Condensation

Pool Boiling

Direct Methanol Fuel Cell

Technical Backgrounds & Design Issues
Wetting of Textured Surfaces: Apparent Contact Angle

\[ \cos \theta_a = \frac{Y_{sg} - Y_{sl}}{Y_{lg}} \]  
(Young's Equation)

- If \( \theta < 90^\circ \): wetting (e.g., water-air-glass)
- If \( \theta > 90^\circ \): non-wetting (e.g., mercury-air-glass)

De-Wetted (Cassie) State

\[ \cos \theta_c = r \Phi \cos \theta_0 + \Phi - 1 \]
\( \Phi \): Fraction of the wetted area
\( r \): Roughness of the wetted area

Wetted (Wenzel) State

\[ \cos \theta_w = r \cos \theta_0 \]
\( r \): Ratio of the actual area to the projected area

Wetting of Textured Surfaces: Contact Angle Hysteresis (CAH)

\( \theta_a \): Advancing contact angle
\( \theta_r \): Receding contact angle

\( \theta_s - \theta_r \): Contact angle hysteresis (CAH)

CAH \( \propto \) Friction (or Pinning, Adhesion)

Furmidge Equation (1962)

\[ F_{adv} = k \bar{w} \gamma (\cos \theta_r - \cos \theta_a) \]
\[ \sin \theta_a = \frac{k \bar{w} \gamma (\cos \theta_a - \cos \theta_r)}{\rho V g} \]
\( k \): Retentive force factor
\( \bar{w} \): Width of a droplet base
\( \gamma \): Surface tension coefficient
\( g \): Gravitational constant
\( \rho \): Density of liquid
\( V \): Volume of a droplet
**Wetting Transition**

De-wetted (Cassie) state  
Composite Interface

Wetted (Wenzel) state  
Homogeneous contact

Evaporation  
\[ \Delta P = \frac{2\gamma}{R} \]

For water droplet:  
\( \Delta P \approx 150 \text{ Pa} \) for \( R = 1 \text{ mm} \),  
\( \Delta P \approx 0.15 \text{ MPa} \) for \( R = 1 \mu \text{m} \)

Hydraulic pressure

And more conditions, e.g., in condensation, under shear flow, etc.

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**Why Nano?:**

To Prevent Wetting Transition

Pillars  
Liquid \((P)_L\)  
Air \((P)_A\)

Pores  
Liquid \((P)_L\)

\[ \rightarrow \text{High-aspect-ratio nano-periodic structures with reentrant sidewall profiles are more desirable for robust de-wetting state.} \]

\[ \rightarrow \text{Discontinuous pore patterns will be more robust than pillar patterns.} \]

Nanomanufacturing Techniques for Large-Area & 3D Nanostructures

Non-Lithographic Techniques: Sol-to-Gel Spray Coating

1. Spin-coating
2. Spray-coating

Suspension of hydrophobic silica NPs

Issue: Lack of pattern regularity over large area
Non-Lithographic Techniques: Sol-to-Gel Spray Coating

Transparent Superhydrophobic Coating

- PMMA glass
- PVC board
- Metal (Al)
- Fabric (Cotton)
- Paperboard
- Wood

Non-Lithographic Nanopatterning Techniques: Maskless Plasma Etching

- Black Silicon (Silicon Grass)
  - Fluorine-based plasma etching

- Polymer nanowires
  - Oxygen plasma etching

*Nanotechnology* 25, 165301 (2014)

⇒ Issue: Lack of pattern regularity over large area
**Lithographic Techniques: Interference (Holographic) Lithography**

**Conventional Lloyd-Mirror Configuration**

\[ p = \frac{\lambda}{2 \sin \alpha} \]

- Pattern Periodicity (or pitch)

Advantages: Low cost, Simple control, Compact

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**Lithographic Techniques: Bosch Reactive Ion Etching Process**

1. **Start with PR Opening**
   - Silicon

2. **Isotropic SF₆ Etch with Anisotropic Bombardment**
   - Scallopimg

3. **Isotropic Polymer Formation with C₄F₆**

4. **SF₆ Etch Again**

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_Nanotechnology_ 17, 5328 (2006)
_Nanostructures in Electronics and Photonics_ (2008)
_Nanotechnology Thought Leaders Series, AzoNano_ (2010)
**Lithographic Techniques:**
Superhydrophobic Surfaces of Sharp-Tip Nanostructures

Fabricated by using laser interference lithography and deep reactive ion etching of Si

All hydrophobic coated with Teflon (< 10 nm thick)

_Nanotechnology_ 17, 5326 (2006)

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**Electrochemical Anodizing for Metallic Substrates:**
Conventional 2D Planar Nanopore Array

Typical Anodizing Setup

Power supply → Electrolyte → Magnetic stirrer

Pore Formation Mechanism

Solution

Overall anodizing reactions: \(2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2\)

a. Pure Aluminum
b. 1st Anodizing
c. AAO removal
d. 2nd Anodizing
e. Pore Widening
**Electrochemical Anodizing for Metallic Substrates:**

**Conventional 2D Planar Nanopore Array**

(Lee et al., 2006, *Nature Materials*)

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**Limitation of 2D Planar Porous Array for Superhydrophobicity**

\[ \cos \theta = \frac{1}{\Phi} \frac{\cos \theta_0 + \Phi - 1}{\Phi} \]

- \( \theta_0 \): Young's contact angle on a smooth surface
- \( \Phi \): Fraction of a solid-liquid wet surface

\[ \Phi = 1 - \frac{2\pi}{\sqrt{3}} \frac{r}{a}^2 \]

- \( r \): Pore radius
- \( a \): Interpore distance

At the maximum pore size \( r = a/2 \), the minimum \( \Phi \) approaches \( \sim 0.1 \) (\( \sim 10\% \)).

- The maximum contact angle expected from the simple (2D planar) hexagonal pore array is not more than \( \sim 162^\circ \).
- The continuous contact line results in larger contact angle hysteresis.
- Hybrid nanostructures (e.g., pillars on pores) will overcome these limits and allow superior superhydrophobicity.

*Schematic (top view) of a unit cell of a hexagonally packed pore array, at the maximum pore size \( r = a/2 \).*

Electrochemical Anodizing for Metallic Substrates: Making Pillar-on-Pore Hybrid Nanostructures

ACS Appl. Mater. Interfaces 4, 842 (2012)
Electrochemical Anodizing for Metallic Substrates: Superhydrophobic Surfaces of Metals

Fabricated by using anodizing techniques of aluminum

Application to Hydrodynamic Friction Reduction
Hydrodynamic Boundary Condition

- Traditional “No-slip” Boundary Condition
  - Bernoulli (1700-1782)
  - Navier (1785-1836)
  - Stokes (1819-1903)

- Phenomenon of Slip
  - Molecular Slip (Intrinsic Slip)
  - Apparent Slip (Effective Slip)

- Dependence on Physical Parameters
  - Surface Wettability and Roughness
  - Dissolved Gas or (Nano)-Bubbles
  - Shear Rate or Pressure Gradient
  - Ionic Strength and Polarity, ...

Microfluidics: Slip or Not to Slip?

\[
Q = \frac{2wh^2 \Delta P}{3 \mu} \quad \text{2lhw} \cdot \gamma \quad \delta = \frac{u_x - u_s}{2wh^2 \Delta P} \quad \frac{h}{3}
\]

Exp. Fluids 34, 635-642 (2003)
Effective Slip

Couette (shear) flow

\[ \delta = b \left( \frac{\mu_s}{\mu_l} - 1 \right) \]

Poiseuille (Pressure-Driven Channel) flow

\[ \Delta P \]

E.g., Liquid: Water (\( \mu_l = 1.0 \times 10^{-3} \text{ Pa} \cdot \text{s at 20°C} \)),
Thickness of Air (\( \mu_a = 1.82 \times 10^{-5} \text{ Pa} \cdot \text{s at 20°C} \)): 1 \( \mu \text{m} \)

\( \rightarrow \) Effective slip length \( \delta \): \( \sim 54 \ \mu \text{m} \) (\( \gg 1 \ \mu \text{m} \)) !!!

Effective Slip on a Superhydrophobic Surface

Cone-and-plate Rheometer

\[ \delta = \frac{K_d}{4} \left( 1 - \frac{3(4\pi - 1/2)}{2\pi} \frac{\mu_s}{\mu_l} - \frac{3}{3} \right) \]

\[ \delta_{\text{emp}} = \frac{0.325}{\sqrt{\dot{\gamma}} - 0.44} \]

Maximizing Slip:
Effects of Pitch and Gas Fraction on Slip

\[ \delta_{\text{grid}} = \frac{p}{\pi} \ln \left( \frac{\pi}{2} \frac{\delta}{\bar{\phi}} \right) \]
\[ \delta_{\text{pore}} = \frac{1}{2} \delta_{\text{grid}} \]

Friction Reduction by Effective Slip

**Couette Flow**

\[ \text{DR}_{\text{Couette}} = \frac{1}{1 + \frac{h}{\delta}} \times 100 \text{ (\%)} \]

**Poiseuille Flow**

\[ \text{DR}_{\text{Poiseuille}} = \frac{1}{1 + \frac{h}{3\delta}} \times 100 \text{ (\%)} \]

Significant skin friction reduction achievable when \( h \sim \delta \)
How about High Reynolds Number Turbulent Flows?

Bare Aluminum (control)  Superhydrophobic (SH) coated  SH Coating-1

Dimension of Aluminum flat plate: LxW=8’x4’

<table>
<thead>
<tr>
<th>Sample name</th>
<th>CA (°) (Ave±SD)</th>
<th>CAH (°) (Ave±SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SH Coating-1</td>
<td>140.3 ± 0.2</td>
<td>6.7 ± 2.5</td>
</tr>
<tr>
<td>SH Coating-2</td>
<td>161.6 ± 0.5</td>
<td>5.3 ± 2.5</td>
</tr>
</tbody>
</table>

CA: Contact Angle, CAH: Contact Angle Hysteresis


Friction Drag in High Reynolds Number Boundary Layer Flow

Lower speed: 1.5 ft/s  High speed: 1.30 ft/s

Issues in High Reynolds Number (High Shear Rate) Flow

After test at low speed

Depleted air bubbles

After test at high speed

Retained air bubbles


Application to Anti-Biofouling
Biofouling Issues

Underwater Vehicles

Oil/Water Pipelines

Using Superhydrophobic Surfaces

Hydrodynamically-Efficient, Antifouling and Anticorrosive Surfaces

- Requirement: Liquid should not fill the gaps.
  - i.e., 1. Surface should be non-wetting.
  - 2. Gaps should be very small. → Nano
  - 3. Tall and slender, sharp-tip structures are preferable.
  - 4. Practical (robust, manufacturable, etc.)
**3D Nanotopography Model Surfaces**

<table>
<thead>
<tr>
<th>Flat</th>
<th>Nanoporous</th>
<th>Nanopillared</th>
</tr>
</thead>
<tbody>
<tr>
<td>As fabricated</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image1" alt="Flat surface" /></td>
<td><img src="image2" alt="Nanoporous surface" /></td>
<td><img src="image3" alt="Nanopillared surface" /></td>
</tr>
</tbody>
</table>

IEEE-NEMS 2014 (Best Student Paper Award)

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**Bacterial Adhesion Test**

![Diagram of bacterial adhesion test setup]

Wall shear rate:

\[ \dot{\gamma} = \frac{3Q}{2(h/2)^2w_0} = 16,000 \text{ s}^{-1} \]

1x1 cm AAO samples

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- 123 -
Bacterial Adhesion Test Results

Hydrophilic Surfaces vs. Hydrophobic Surfaces
Application to Anti-Corrosion

Issues of Corrosion

- 1-5% GNP (Gross National Product) loss: $276B (USA)
- Environment and durability issues in current technologies for corrosion prevention (Painting, Coating, Cathode Protection, etc.)
Using Superhydrophobic Surfaces

Hydrodynamically-Efficient, Antifouling and Anticorrosive Surfaces

- Requirement: Liquid should not fill the gaps.
  i.e., 1. Surface should be non-wetting.
  2. Gaps should be very small. → Nano
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Model Surfaces

- : Aluminum
- : Anodized Aluminum
- : Teflon

Bare Aluminum (Bare Al)

Anodized Aluminum (20-150: Pore size - Oxide thickness)

Teflon-Coated Bare Aluminum (TBare Al)

Teflon-Coated Anodized Aluminum (T20-150)
**Potentiodynamic Polarization Results**

**Polarization Test (1-h immersion)**

![Graph showing polarization test results with different samples: Bare Al, Anodized Al (T20-150), Teflon Bare Al (T150), and Teflon Anodized Al (T20-150).]

**Corrosion Inhibition Efficiency (IE, %)**

![Graph showing corrosion inhibition efficiency with samples immersed for 1 hour.]

The value of $E_{corr}$ shifts positive direction with the lower value of $I_{corr}$ → Enhanced corrosion resistance.

Bare Al < Anodized Al < Teflon Bare Al < Teflon Anodized Al

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**Effect of Oxide Layer Thickness and Pore Size**

![Imagenes mostrando la evolución de la capa de óxido y el tamaño de los poros en diferentes muestras.]

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>T20-150</th>
<th>T80-150</th>
<th>T20-500</th>
<th>T80-500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore size (nm)</td>
<td>20</td>
<td>80</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>Oxide layer thickness (nm)</td>
<td>150</td>
<td>150</td>
<td>500</td>
<td>500</td>
</tr>
</tbody>
</table>
**Effect of Oxide Layer Thickness and Pore Size**

**Polarization Test**

(3.5% NaCl)

**Corrosion inhibition efficiency (IE)**

More enhanced corrosion resistance with larger pore and thicker oxide layer !!

**Durability**

- Teflon-coated nanoporous anodic alumina surfaces show good stability/robustness for the corrosion inhibition efficiency.
- Teflon-coated nanoporous anodic alumina surfaces with larger pore size and thicker oxide layer show better corrosion resistance and inhibition efficiency.
Application to Anti-Icing

Issues of Icing

Aviation

Wind turbine

Transportation

Power Transmission
Icing Wind Tunnel at Stevens

<table>
<thead>
<tr>
<th>Temperature</th>
<th>-35°F to ambient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Size, Max Velocity</td>
<td>8&quot;x8&quot;, 35 MPH</td>
</tr>
<tr>
<td></td>
<td>&lt; 3.5&quot;x3.5&quot;, 80 MPH</td>
</tr>
<tr>
<td>Liquid water content (LWC)</td>
<td>0.2 - 3 gm²</td>
</tr>
<tr>
<td>Mean volumetric diameter (MVD)</td>
<td>20 - 50 microns</td>
</tr>
</tbody>
</table>

a) Tunnel prior to insulation.
b) Liquid nitrogen connected to an evaporator.
c) Control panel and electronic housing unit.
d) Test section containing a CCD camera and a sample.

http://me424iw.wordpress.com

Colloid Polymer Sci. 291, 427 (2013)

Superhydrophobic Surface Samples

<table>
<thead>
<tr>
<th>SH Sample Name</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Roughness Scale</td>
<td>Micro</td>
<td>Micro</td>
<td>Nano</td>
<td>Nano</td>
</tr>
<tr>
<td>Apparent Contact Angle (CA)</td>
<td>165 ± 1°</td>
<td>165 ± 1°</td>
<td>169 ± 3°</td>
<td>170 ± 3°</td>
</tr>
<tr>
<td>Advancing Contact Angle</td>
<td>166 ± 3°</td>
<td>166 ± 2°</td>
<td>169 ± 3°</td>
<td>170 ± 2°</td>
</tr>
<tr>
<td>Receding Contact Angle</td>
<td>150 ± 3°</td>
<td>158 ± 3°</td>
<td>163 ± 2°</td>
<td>167 ± 1°</td>
</tr>
<tr>
<td>Contact Angle Hysteresis (CAH)</td>
<td>16 ± 3°</td>
<td>8 ± 6°</td>
<td>7 ± 5°</td>
<td>3 ± 1°</td>
</tr>
</tbody>
</table>

Coatings from Ross Nanotechnology
Anti-Icing in Dynamic Flow Conditions

Temperature: -6 °C, Velocity: 25 MPH, Time lapse: 0-300 sec

Colloid Polymer Sci. 291, 427 (2013)

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Anti-Icing: Effects of Contact Angles

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<td>3 ± 1°</td>
</tr>
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The superhydrophobic coating with the lowest contact angle hysteresis (CAH) results in the best anti-icing effect (longest delay time against icing).

Colloid Polymer Sci. 291, 427 (2013)
**Ice Morphology: Fakir State of Ice**

Bare (uncoated)  Superhydrophobic coated

In 240 seconds

**De-Icing Efficiency**

After forming a thin ice layer on the superhydrophobic surface sample:

1) Vibration, Icing temperature: 20°F (-6 °C)

2) Melting on a hand, Icing temperature: 14°F (-10 °C)

→ Superhydrophobic surfaces help not only anti-icing but also de-icing!
Concluding Remarks

- Micro- and nano-patterned surfaces of well-tailored geometrical three-dimensionality, surface energy, and mechanical pliability can provide novel multi-functional material properties, which will enable many new scientific quests and engineering applications.

- Development of more efficient, e.g., low-cost, high-rate, large-area, 3D, and well-regulated nanomanufacturing technologies is essential for the systematic studies and practical applications.

- Active mechanisms should be incorporated to the passive nano-textured surfaces for more robust and sustainable applications.

- Mechanical robustness (wear and abrasion) is another issue to be considered.

Thank you.
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