

6/4/2012

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NASA Aeronautics Mission Directorate FY11 Seeding Phase I Technical Seminar

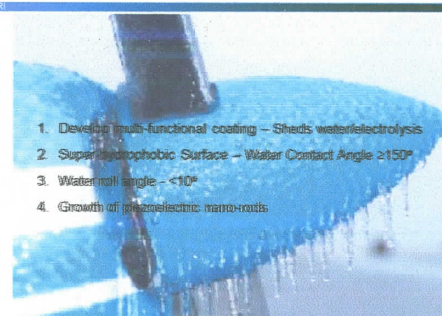
Nano-Rod Piezoelectrics for Icephobic Surfaces

Frederick Dynys (NASA-GRC), Eric Kreeger (NASA-GRC) & Alp Sehirlioglu (CWRU)

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Objectives

1. Develop multi-functional coating – Shields water/electrolysis
2. Superhydrophobic Surface – Water Contact Angle $\geq 150^\circ$
3. Waterfall angle - $< 10^\circ$
4. Growth of piezoelectric nano-rods

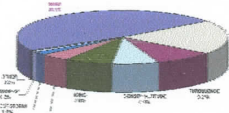


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Weather Related Accidents

NTSB Weather Related Accidents 1994 - 2003



- Ice accretion disrupts airflow reducing lift and increasing drag
- Ice also can form in the engine intake, blocking air flow to the engine

Anti-Icing
Proscriptive: before the flight enters icing conditions: thermal heat, prop heat, pitot heat, fuel vent heat, windshield heat, and fluid surface de-icers

De-icing
Reactive: ice build up includes surface de-ice equipment such as boots, sweeping wing systems, and heated wings


- 19,562 total accidents
- 4,159 (21.3%) weather related
- 291 (7%) cause by icing

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Flight Operations

- Iceing Conditions Disrupt Flight Schedules
 - Average cost for idling aircraft - \$45/minute
 - Flight delays cost the airline industry - \$19 billion/yr
- On Ground Airframe De-icing
 - 200-600 million gallons of Aircraft Deicing Fluid (ADF)/yr
 - ADF cost is \$11-\$18/gallon
 - ADF environmental pollutant - 22 million gallons release
 - EPA imposing effluent discharge standards
 - Corrosion of aircraft parts
 - Deterioration of carbon brakes

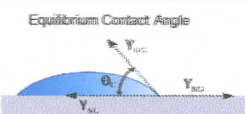


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Basics of Wetting

Equilibrium Contact Angle



γ_{SL} : solid-liquid surface tension
 γ_{SG} : solid-gas surface tension
 γ_{LG} : liquid-gas surface tension

Young Dupré relation

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

Smooth surfaces exhibit maximum contact angles ~ $120^\circ - 130^\circ$

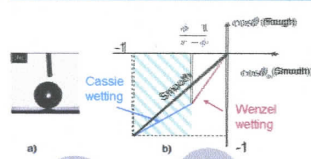
Wetting Regimes

Hydrophilic $\theta = 0^\circ$	Partially Wetting $\theta < 90^\circ$	Hydrophobic $\theta > 90^\circ$	Super-Hydrophobic $\theta > 150^\circ$
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Basics of Wetting



R. N. Wenzel, 1936
 $\cos \theta_w = r \cos \theta$
 θ_w : CA on the rough surface
 θ : CA on the smooth surface
 r : roughness factor ($r > 1$)
 Real Area/Flat Area

A. B. D. Cassie, 1948
 $\cos \theta_c = f_1 \cos \theta - f_2$
 θ_c : CA on the rough surface
 θ : CA on the smooth surface
 f_1 : fraction of solid
 f_2 : fraction of air ($f_1 + f_2 = 1$)

Surface roughness enhances hydrophobicity

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Super-Hydrophobic Surfaces

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Why Super-Hydrophobic Surfaces

Water Droplet (Bouncing)

Superhydrophobic (WCA=102°)
Superhydrophobic (WCA=151°)
Hydrophobic (WCA=65°)

Colin R. Crick - Ph. D. Thesis - University College London - 2011

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Why Super-Hydrophobic Surfaces

Low Roll Off Angles < 10°

Hysteresis $H = \theta_A - \theta_R$
Small Hysteresis

Liquid droplet can roll off easily

Icing

Lowers Adhesion Strength

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Super-Hydrophobic Surfaces - Deficiencies

Water Condensation Frost

WCA Dependency

Pressure
Evaporation
Droplet Size

Droplet Impact

Once ice forms - Superhydrophobic surface cannot repel ice growth

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Ice Electrolysis

Petrenko - Dartmouth

10 s after 6 volts
T = -10 °C

Electroplated Copper Grid Electrodes

~Small bubbles generated at the interface by ice electrolysis $H_2O \rightarrow H_2 + O_2$

- Reduces the ice adhesion by 10 times at 21 V @ 30 s.
- AC more efficient than DC

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Innovation Multi-Functional Coating

Super Hydrophobic Surface + Electrolysis Function → Multi-Functional Coating

Provides 2 mechanisms to mitigate icing

Phase I Concept

Piezoelectric Fibers

Energy Harvesting

Self Powered - Piezoelectric

Drive Electrolysis - ZnO/Water

Super Hydrophobic - ZnO

Icing - ZnO - Delayed Freezing -90 min @ -5 °C

He et al. - Beijing Nat Lab 7/2011

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ZnO Coating Technical Approach

ZnO Nano-rod Fabrication

2 inch Si Wafers

Urea

$$(CH_2)_6N_4 + 6H_2O \xrightarrow{\Delta} 6CH_2O + 4NH_3$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$2OH^- + Zn^{+2} \rightarrow ZnO(s) + H_2O$$

Tasks for Phase I:

- Processing/characterization of ZnO nanorods - completed
- Procurement/development - completed
- Fabrication/icing chamber - completed
- Measure contact angles of static water droplets - completed
- Testing/icing chamber - in progress

Modify optical system for detecting ice formation.

Goniometer / Tensiometer

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ZnO Coating

Experimental

Seed Layer	Substrate	Zn Salt	Hydrolysis	T (°C)	Time (hrs)	WCA (°)	WCA Ratio	
Colloidal ZnO	Si	Zn Nitrate	HMTA	90	4	1		
ZnO via Zn Acetate	Si	Zn Nitrate	HMTA	90	4	1		
PVD ZnO	Si	Zn Nitrate	Zn Chloride	Zn Acetate	HMTA	90	4, 14, 72	1, 1.25, 1.5, 2, 2.3
						90	4	1
Colloidal Ag	Si	Zn Nitrate	HMTA	90	4	1		
PVD Ag	Si	Zn Nitrate	HMTA	90	4	1		
Carbon Nanotubes	Si	Zn Nitrate	HMTA	90	4	1		
PVD Zn	Si	Zn Nitrate	HMTA	90	4	1		
Colloidal EYO	Si	Zn Nitrate	HMTA	90	4	1		
None	Si	Zn Nitrate	HMTA	90	4	1		

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PVD ZnO Seeds

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Colloidal Seeds

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Thermal/Etching/SAMs Treatment

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Lotus Effect

Stainless Mesh
~100 mm holes - hexagonal
~SAMs 126°
heptadecafluoro-1,1,2,2-tetrahydrodecyl-triethoxysilane

Silicon

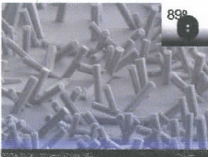
Surface	WCA
Untreated Si	34.7
Polished	23.8
Rough	98.8

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Carbon Nanotubes

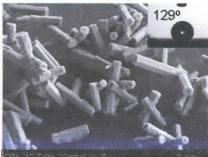
WCA for CNT Coating 143.2°

Metal Coated Substrate



89°

CNT Coating

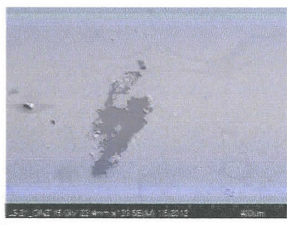


129°

Metal Catalysis act as nuclei for ZnO Growth

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Mechanical Robustness



- Mechanical robustness – poor
- Film fails upon touching
- Films required gentle handling and washing
- Film porosity is needed for super hydrophobic structure

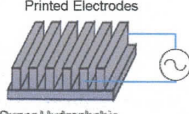
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Phase II

Super Hydrophobic Surface + Electrolysis Function → Multi-Functional Coating
Provide 2 mechanisms to mitigate ice

Improve mechanical properties → Carbon Nanotube/PEDOT/PSS composite
Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)

Printed Electrodes



Super Hydrophobic Electrode Pattern

Goals

- Structure Beads Water
- Structure Sheds Water
- Reduce Power Consumption
- Electrolysis of Ice/Water
- Mechanically Robust
- Easy to Fabricate

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Summary

- Proposed concept for multi-functional coating still valid
- Completed phase I tasks
- Successively Grown ZnO nano-rods
- Successively Characterized Wetting Behavior – 147°
- Environmental Chamber - -30°C/Humidity/WCA
- ZnO nano-rods exhibit poor mechanical properties
- Phase II re-focused on mechanical robustness of coating
- Technology – TRL 1 to TRL 2
- Information Dissemination – Conference, Publication

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