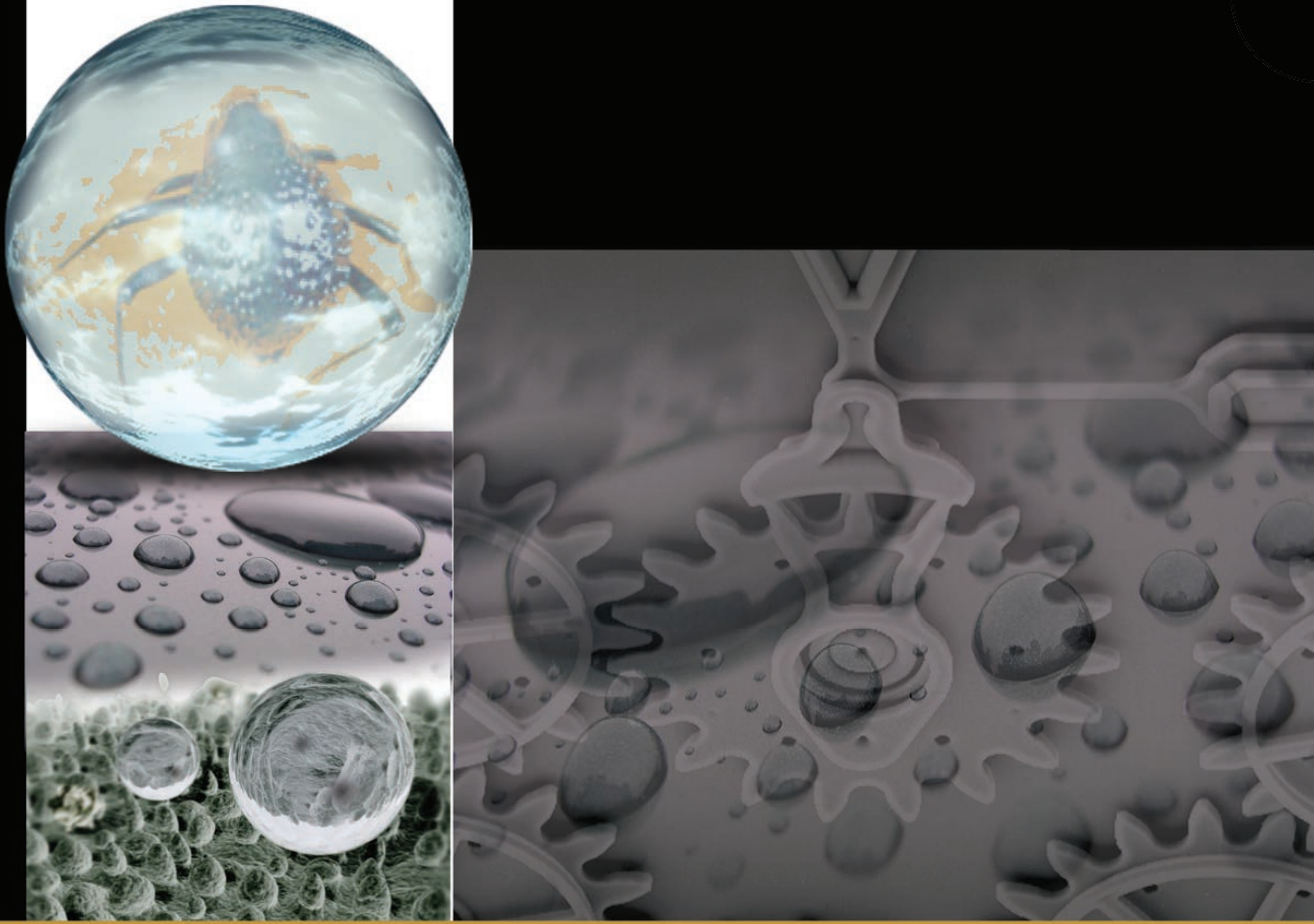
2008 R&D 100 Award Entry Form

SUPERHYDROPHOBIC COATING

Sandia
National
Laboratories



Submitting Organization

Sandia National Laboratories
P.O. Box 5800, MS 1349
Albuquerque, NM 87106

C. Jeffrey Brinker
Phone: 505-272-7627
Fax: 505-272-7336
cjbrink@sandia.gov

AFFIRMATION: I affirm that all information submitted as a part of, or supplemental to, this entry is a fair and accurate representation of this product.

C. Jeffrey Brinker

Joint Entry

N/A

Product Name

Superhydrophobic Coating

Brief Description

A patternable superhydrophobic coating that can be applied to any substrate using numerous simple procedures.

Date When First Marketed or Available

First marketed on July 12, 2007.

Inventor or Principal Developers

C. Jeffrey Brinker, Sandia Fellow
Sandia National Laboratories
1001 University Blvd., Suite 100
Albuquerque, NM 87106
Phone: 505-272-7627
Fax: 505-272-7336
cjbrink@sandia.gov

Inventor or Principal Developers

Eric Branson, Technologist
Sandia National Laboratories
1001 University Blvd., Suite 100
Albuquerque, NM 87106
Phone: 505-272-7637
Fax: 505-272-7336
edbrans@sandia.gov

David J. Kissel, Graduate Student
Sandia National Laboratories
University of New Mexico Dept. of Nanoscience and Microsystems
1001 University Blvd., Suite 100
Albuquerque, NM 87106
Phone: 505-272-7343
Fax: 505-272-7336
dkissel@unm.edu

Adam Cook, Student Intern
Sandia National Laboratories
1001 University Blvd., Suite 100
Albuquerque, NM 87106
Phone: 505-272-7663
Fax: 505-272-7336
acook@sandia.gov

Seema Singh, Technical Staff
Sandia National Laboratories
7011 East Ave.
Livermore, CA 94550
Phone: 925-294-4551
seesing@sandia.gov

Product Price

Approximately $10/gallon

Patents or Patents Pending

Pending Patent–Application # 11/104,917

Primary Function

Quite often, Nature has a way of designing biological structures to solve challenging engineering problems. Some familiar examples are the various ways in which plants and animals cope with either the abundance or scarcity of water. Figures 1 and 2 showcase two important natural examples of superhydrophobic materials, which have served to inspire this product. The Lotus leaf's hierarchical roughness and surface chemistry confer to the leaf superhydrophobic properties; that is, water drops adopt a contact angle greater than 150° and roll like marbles under the gentlest forces causing self-cleaning.

During occasional fogs, water drops nucleate on water-loving pads on the back of the Namib Sternocara Desert beetle. The drops grow and spread onto adjacent superhydrophobic regions allowing the beetle to tip its body and roll the water to its mouth for drinking. The principle that both surface roughness and surface chemistry can be used to amplify water repellency was the basis for this product's material engineering.

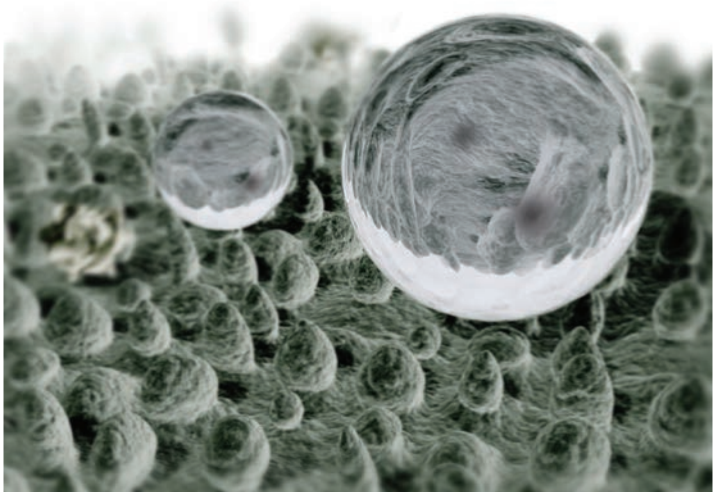


Figure 1:
An environmental scanning electron micrograph image of the famed Lotus leaf—water droplets adopt an almost spherical shape on the waxy protrusion of the leaf surface.

Computer graphic of 'Lotus Effect'
wthielicke.gmxhome.de

Figure 2:
The Namib Sternocara Desert beetle lives in one of the driest regions on earth and uses a patterned superhydrophobic surface to harvest water.

2008 R&D 100 Award Entry Form

Primary Function

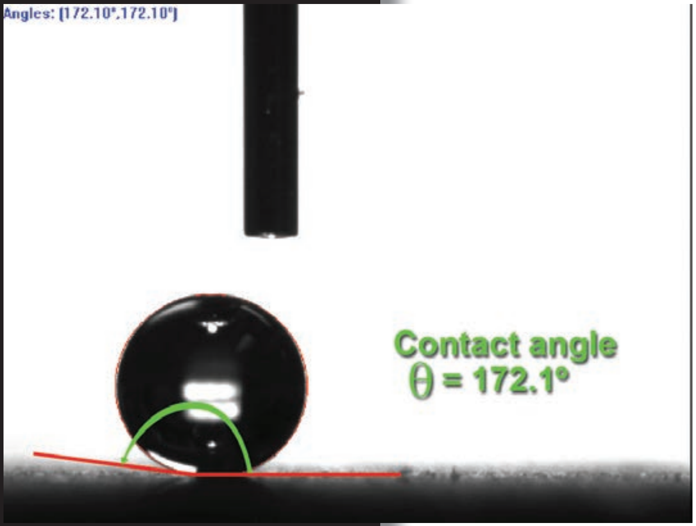


Figure 3:
A microliter of water forms nearly a perfect sphere on the surface of this coating product.

Inspired by the Lotus leaf and the desert beetle, our process uses sol-gel chemistry (Brinker and Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press 1990) to make a coating solution, which upon simple evaporative drying, develops a nanoscopically rough silicon dioxide surface decorated with hydrophobic ligands. This combination of surface roughness and surface chemistry confer to the surface superhydrophobic properties as seen in Figure 3, where a water droplet is measured to have a 172° contact angle, θ.

Importantly, this superhydrophobic coating process can be applied to any surface regardless of composition and can be applied to complex geometries. Additionally, by nanoscale control of the surface roughness, our coating exhibits nearly perfect optical clarity (see Figure 4). Optical transparency is a must for applications like self-cleaning, non-fogging displays, avoiding ice formation on optical elements, and protecting culturally important statuary from acid rain corrosion. *Ultra-high contact angles combined with optical transparency and the ability to coat to arbitrary surfaces are distinguishing features of this technology.*

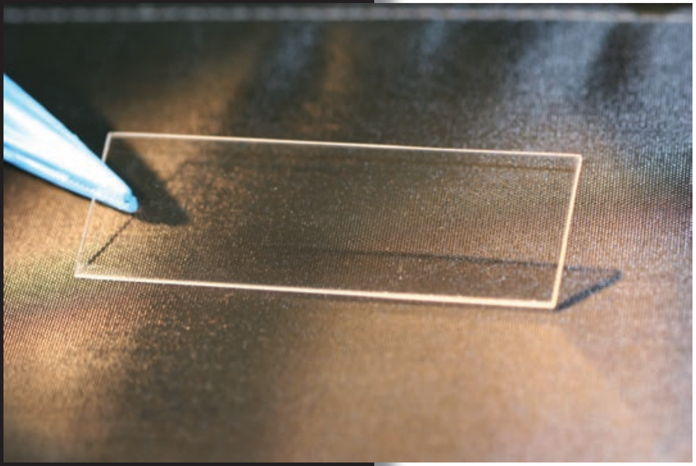


Figure 4:
The optical clarity of our product is evident from this superhydrophobic coated glass slide.

The patterned back of the Namib beetle inspired another characteristic of this product: the ability to selectively pattern the coating and spatially control the wetting behavior for a desired application. Exposure to high-intensity, low-wavelength UV light under special conditions allows us to continuously vary the contact angle from over 170° to 0°. This means we can define with light the pathways along which water droplets will roll—important for droplet-based fluidic architectures. Within a microfluidic device, we can control whether water sticks to or slips at the surface. We can define water corrals (adjacent isolated water reservoirs) useful for drug screening, biological studies, and combinatorial chemistry. And, similar to the Namib beetle, we can develop water collection systems. Figure 5 shows a superhydrophobic film patterned with a square array of hydrophilic (water-loving) patches. These patches were made by exposure to UV light through a photomask. In the UV-exposed regions, hydrophobic ligands are progressively converted to hydrophilic regions reducing the contact angle. Exposure of this patterned surface to high humidity causes water drops to nucleate on the hydrophilic patches. These patches grow into drops, which extend onto the surrounding superhydrophobic material. When the drops have grown to a sufficiently large size, gravity causes them to detach and roll, allowing collection. Implemented on tents or the walls of huts, this technology makes possible the ability to provide pure water throughout the world with the use of no energy.

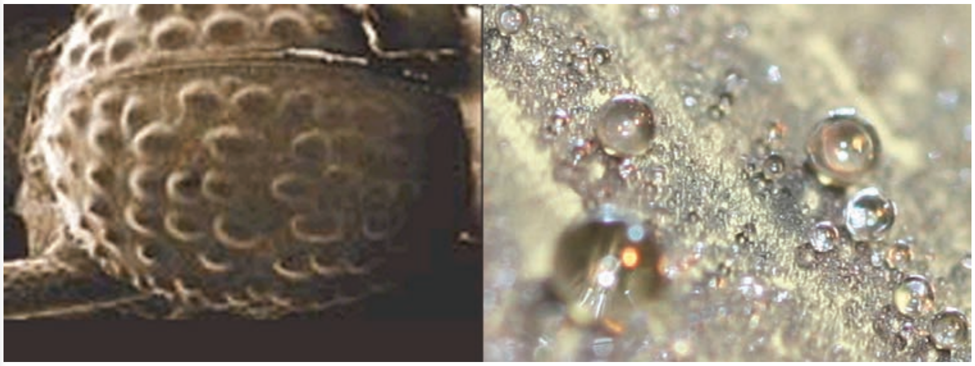


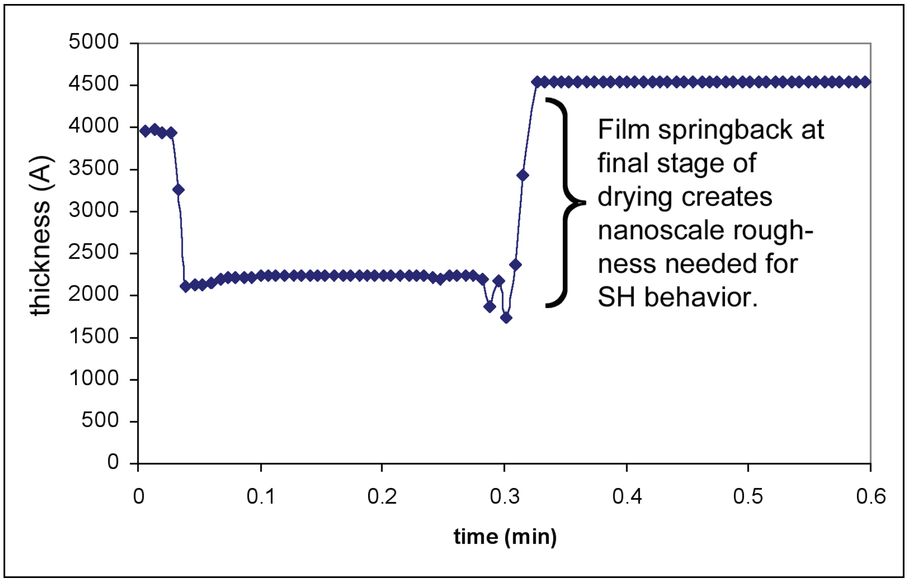
Figure 5:
Shown is a picture of a patterned thin film of the product (right). UV exposure created an array of hydrophilic patches surrounded by superhydrophobic (SH) regions. Upon exposure to a stream of water, vapor water droplets nucleate and grow on the hydrophilic patches extending onto the surrounding SH regions. Tilting of the sample causes water to roll allowing collection. The collected water appeared only after a few minutes of exposure to water vapor. The pattern on the Namib Stenocara beetle (left) was the inspiration for the choice of the pattern.

The absolutely unique and essential feature of this coating process is that unlike conventional coating systems, which shrink continuously during drying to produce low-porosity films, this coating springs back (expands) to a lower density state during the final stage of drying. This process is shown in Figure 6, which plots the film thickness during drying measured by a standard optical technique called ellipsometry. It is observed that the film shrinks initially due to solvent loss and development of drying stress, but at the final stage of drying, it expands to nearly twice its fully shrunken thickness. The resulting structure is highly porous, as is shown by the transmission electron micrograph in Figure 7. Typical values for the refractive index of the material range from 1.05 to 1.12 at a wavelength of 600 nm (the refractive index of air is 1.00). This "spring back" effect is important because it creates the nanoscale roughness needed to develop the superhydrophobic effect. It occurs because a hydrophobic silicon dioxide nanostructured network forms during drying.

Primary Function

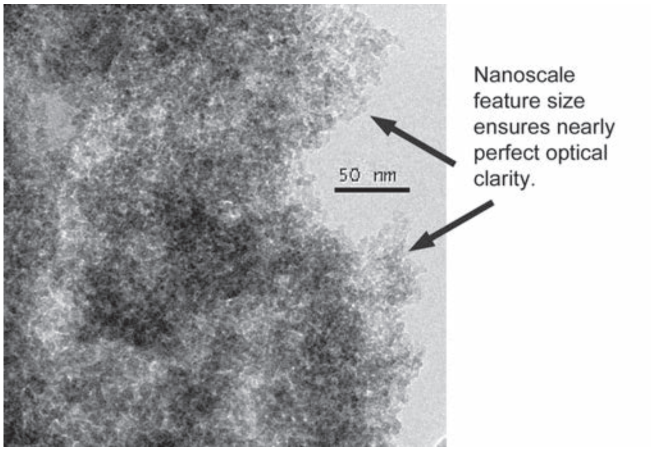
This network expands like a spring at the final stage of drying when the drying stresses vanish. No other coatings known exhibit this unique springback behavior

Essentially any standard coating method can be used for this product including spin-coating, dip-coating, aerosol spraying, and ink-jet printing. The material retains its superhydrophobic properties at temperatures up to 450°C. UV patterning, exposure to short wavelength UV light through a photomask, allows the contact angle to be varied continuously from 170° to 0° depending on the exposure time. This ability to control the material's affinity for water in a spatially defined manner represents a unique and distinguishing attribute of our coating product. (Films remained stable for years under normal illumination.)



Film springback at final stage of drying creates nanoscale roughness needed for SH behavior.

Figure 6:
In situ ellipsometric data of the superhydrophobic coating solution as it dries at room temperature showing the change in film thickness during drying. The film initially thins due to solvent evaporation and drying stress, but after about 20 seconds, the film thickness increases as the nanostructured silica expands to form a nanoporous film upon final drying. The final thickness of this film was 466 nanometers.



Nanoscale feature size ensures nearly perfect optical clarity.

Figure 7:
A TEM image of the superhydrophobic coating material. The differences in contrast clearly show the porous nature of the structure at the nanoscale.

Competition

We can only find two superhydrophobic patent applications, although there are literature descriptions of other SH coating processes (see table on page 11).

Coating 1 – Application Number: 10/912,576

This is a superhydrophobic coating based on the deposition of polyelectrolyte multilayers accomplished by multiple successive dipping steps (10 -100) of a substrate into an aqueous polycation solution (poly-allylamine hydrochloride) and an aqueous polyanion solution (poly-acrylic acid). During each dip, a monolayer is deposited onto the substrate. This coating changes the net surface charge so that when the substrate is dipped into the alternate solution, the growing film electrostatically attracts a monolayer of the other solution. This continuous alternation of solutions results in a multilayed film. These films must be further processed by immersions into low pH solutions followed by nanoparticle deposition imparting the surface roughness required to achieve superhydrophobicity. The films are then heated to 180°C for a few hours for cross-linking. Once the film is crossed-linked, SiO_2 particles are deposited onto the film by alternately dipping into an aqueous polycation solution and an aqueous suspension of negatively charged nanoparticles. When the desired multilayer height is achieved; the film undergoes its final dipping into the nanoparticle suspension. The film is then subjected to chemical vapor deposition (CVD) of (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane followed by a few hours of heating at 180°C giving a final film contact angle of 172º.

This is an extremely complex process. Building films layer by layer and having to impart the surface roughness and low surface energy required for superhydrophobicity in additional separate coating steps is time consuming, expensive, and does not allow for film deposition in a manner other than dip-coating. The substrate material is limited in size because of the need to be dip-coated and also limited by the requirement to withstand two separate 180°C heating steps. This technique also lacks the ability to adjust or pattern the films contact angle after coating.

Coating 2 – Application Number: PCT/AU2004/000462

This is a superhydrophobic coating based on a mixture of particulate material (hydroxyl terminated silica particles), a chemical modifying reagent (imparting hydrophobicity on the particulate material), a linking agent (which allows for the formation of polymer strands between two of more particulate materials and the formation of polymer strands between particulate materials and the substrate surface), a cross-linking catalyst (peroxide, platinum, tin, or zinc is added to catalyze the crosslinking reaction), and toluene or hexane. This mixture is then applied to a substrate by either spray coating or brushing. The films are then allowed to cross-link for several hours at room temperature or at temperatures below 150°C for a few hours. A final film contact angle of 169° can be achieved.

This process normally uses heavy metals as catalysts, which regardless of concentration are bad for the environment, often bio-incompatible and expensive to manufacture. After deposition the film must further crosslink for several hours, which extends the overall coating time and limits its use in some areas. The particulate nature of the film causes it to be translucent or opaque. This technique also does not allow for the ability to alter the films contact angle after coating.

Comparison Matrix

The provided matrix lists various superhydrophobic materials found in the literature and their properties and processing requirements. When summarized in this way, it is easy to compare and recognize the benefits of our simple sol-gel coating. Our coating requires no surface pretreatment before deposition and can be applied to any substrate, including objects possessing complex geometries. Whether applied by spin-coating, spray-coating, dip-coating, or ink jet printing, the superhydrophobic properties and near-perfect optical clarity can be observed immediately after deposition without any further modifications. An added and technologically significant feature of this coating is its ability to be engineered to achieve any contact angle from 170º to 0º.

Coating Method	Contact Angle (deg)	Substrate Pretreatment	Deposition	Surface Modification	Tunable CA	Patternable	Transparent
Plastic Transformation	160	unknown	dropwise / 130°C vacuum oven	rapid cooling from 130°C to 70°C	No	No	No
Carbon Nanotube Forest	170	Ni catalyst islands IN PECVD @ 650°C	plasma discharge acetylene/ammonia	HFCVD coating @ 500°C	No	No	No
Polyelectrolyte Multilayers	172	acidic soakings	100+ dip coatings	CVD @ 180°C / 2hrs	No	Yes	No
Galvanic Cell Reaction	154	ultrasonic washings in acetone and ethanol	$AgNO_3$ and HF immersion	dodecanethiol soaking overnight	No	No	No
Nanosphere Lithography	168	unknown	spin coating	Oxygen Plasma / Ag deposition / octadecanethiol rinse	132º - 170º	No	No
Sol-Gel Foam	160	no substrate	no deposition	Heated @ 300°C	No	No	No
Sol-Gel Alumina	160	Al_2O_3 heated to 400°C + immersion in boiling water	dip coating	heptadecafluorodecyl-trimethoxisilane	5º - 160º	Yes	No
Coating 1 (10/912,576)	172	acidic soakings	10-100+ dip coatings w/ Si particles 0.2-20 microns in diameter	CVD @ 180°C / 2hrs	No	Yes	No
Coating 2 (PCT/AU2004/000462)	165	unknown	spray, spin, dip with hexane solvent	Room temp (days) or 150°C (hours) heating for crosslinking of the polymer strands	No	No	Translucent or opaque depending on size of particular material
Our Simple Sol-Gel Coating	172	None	spray, spin, dip	None	0º - 170º	Yes	Yes

Why Superhydrophobic Coating is Better than the Competition

Although there are a wide range of commercially available hydrophobic coatings, there exist almost no superhydrophobic coatings (water contact angles greater than 150°.) Most coatings of this type are classified as only being hydrophobic rather than superhydrophobic. The distinction is made by water contact angles exceeding 150° for superhydrophobic materials. Contact angles below this value render a material hydrophobic rather than superhydrophobic, and water tends not to roll as droplets. Our product improves upon the remotely competitive products in its extreme water repellency. Also, most superhydrophobic materials that have been developed are opaque or translucent: none possess the optical clarity of our product. In addition, the other materials that have been developed seem to be confined to research and academia only; however, this product is at the stage of commercial use and is available.

The main advantage of our product is that it is simple to prepare and apply compared to the existing competitor's procedures. Our superhyrdophobic surfaces develop from a very low-viscosity sol by the formation of a silicon dioxide nanostructure and its expansion/springback at the final stage of drying. This makes our procedure amenable to coating small features and virtually any kind of substrate. Applied to plastic, glass, paper, textile, and silicon substrates, our superhydrophobic coatings are optically transparent with contact angles exceeding 170°. In addition, we have developed a technique enabling spatially defined, continuous optical adjustment of the water contact angle from 0° to 170°. Also with a silyation treatment after UV/Ozone exposure, we can largely reverse the effect of the UV/Ozone treatment (Figure 8)– effectively erasing the pattern.

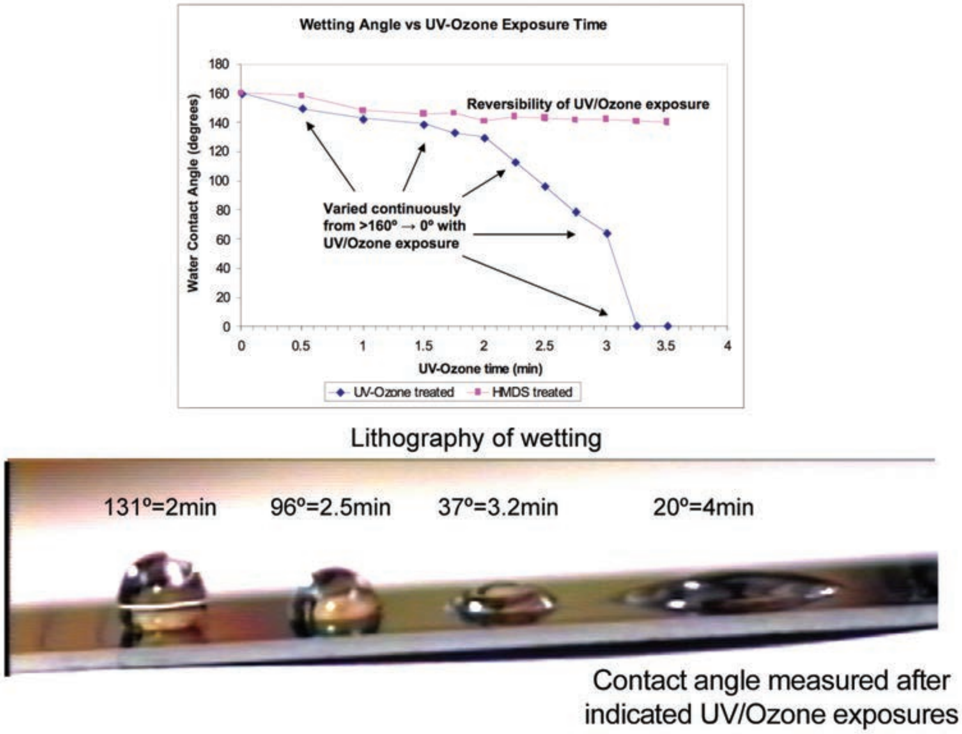


Figure 8: (Top) blue line–contact angle versus time showing lower contact angles over time spent in UV/Ozone treatment. Pink line–shows the ability to reverse the effects of the UV/Ozone treatment on the same film exposed in the blue line. (Bottom) shows various contact angles achieved on a single film.

Principal Applications and Other Applications

By patterning hydrophilic pads surrounded by a superhydrophobic surface on a sheet of plastic or fabric, we expect to be able to provide low-cost water collection surfaces to countries where availability of drinkable water is in jeopardy.

Because our approach comprises a simple spray-, dip- or spin-on approach to develop an immediate, transparent superhydrophobic surface on arbitrary substrate compositions, shapes, and topologies, the applications of this product are extensive. First, it presents a viable solution for the prevention of moisture buildup. Immediately, this dramatically reduces the rates of corrosion of metal even under the highly corrosive conditions of salt fog (see paper on *Corrosion Science* in Appendix B). Moreover, it can be applied simply to microelectronic devices, microelectromechanical devices (MEMS), optics, medical devices, textiles, and antiquities. In these cases the superhydrophobic effect would prevent corrosion, avoid sticking of MEMS due to capillary condensation, prevent ice formation on optical elements, avoid bio-fouling, effect a breathable superhydrophobic fabric, and arrest acid rain corrosion of limestone and marble artifacts. Preservation of our cultural heritage in objects constructed of stone is a particularly crucial issue with worldwide impact. Here the requirement is a coating that is completely "invisible." The ultra-low refractive index of our coating ($n < 1.05$ compared to air $n = 1.00$) means that our material effectively disappears in air, satisfying this criterion. Transparency combined with superhydrophobicity may allow our material to arrest the corrosive action on outdoor antiquities. Acid rain corrosion, which has been extensive since the Industrial Revolution, has virtually eradicated all artistic details on much limestone and marble in Europe and Asia .

The self-cleaning characteristic, or lotus effect, of this coating makes it suitable for rendering a surface antimicrobial. Water's ability to slide without resistance on this product opens the door for the reduction of the energy required to pump fluids in pipe networks. Its extremely low density makes it a good candidate for applications in avionics as a moisture barrier or an ice resistant material. Since the product can be applied using aerosol technology, it would be possible to market it as a protective coating for paint, furniture, art, and many other items. Finally, there is the ability to pattern the material to develop a synthetic water harvesting surface mimicking that of the Namib Desert beetle. By patterning hydrophilic pads surrounded by a superhydrophobic surface on a sheet of plastic or fabric, we expect to be able to provide low-cost water collection surfaces to countries where availability of drinkable water is in jeopardy. These surfaces would collect pure water, which would not be susceptible to pollution or disease. In general, where there is a need to control wetting our product can be used.

Summary

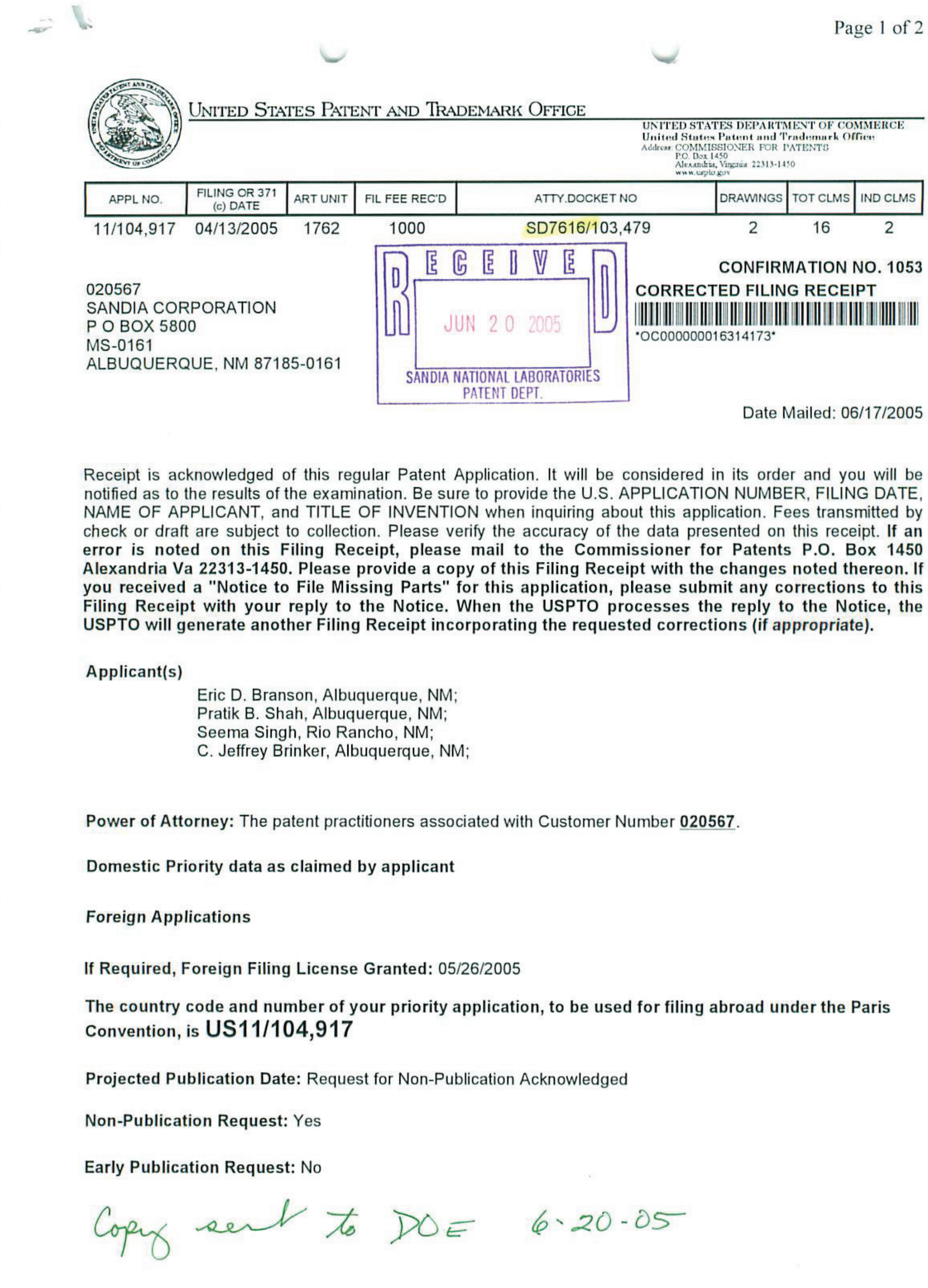
In situations where moisture has been an unconquerable enemy, this product presents a solution that has never before been available commercially.

Our superhydrophobic process allows the immediate formation of transparent superhydrophobic coatings on arbitrary surface compositions, shapes and topologies. The superhydrophobic surface has a water contact angle much greater than 150°, has self-cleaning properties, and is invisible to the naked eye. Water is not merely repelled; it literally jumps / bounces off of the coating. In situations where moisture has been an unconquerable enemy, this product presents a solution that has never before been available commercially. The importance of this product abounds from its potential to prevent corrosion, conserve energy of pumping fluids, protect electronics and antiquities, avoid the buildup of ice on aircraft, and provide a new approach to water collection where the availability of drinking water is at great risk.

Contact Person for Arrangements

Robert W. Carling, Director
Sandia National Laboratories
PO Box 969
Mail Stop 9405
Livermore, CA 94551-0969
925-294-2206 (phone)
925-294-3403 (fax)
rwcarli@sandia.gov

Pending Patent—Application # 11/104,917



UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPL NO.	FILING OR 371 (c) DATE	ART UNIT	FIL FEE REC'D	ATTY.DOCKET NO	DRAWINGS	TOT CLMS	IND CLMS
11/104,917	04/13/2005	1762	1000	SD7616/103,479	2	16	2

020567
SANDIA CORPORATION
P O BOX 5800
MS-0161
ALBUQUERQUE, NM 87185-0161

RECEIVED
JUN 20 2005
SANDIA NATIONAL LABORATORIES
PATENT DEPT.

CONFIRMATION NO. 1053

CORRECTED FILING RECEIPT

OC000000016314173

Date Mailed: 06/17/2005

Receipt is acknowledged of this regular Patent Application. It will be considered in its order and you will be notified as to the results of the examination. Be sure to provide the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION when inquiring about this application. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please mail to the Commissioner for Patents P.O. Box 1450 Alexandria Va 22313-1450. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections (if appropriate).**

Applicant(s)

Eric D. Branson, Albuquerque, NM;
Pratik B. Shah, Albuquerque, NM;
Seema Singh, Rio Rancho, NM;
C. Jeffrey Brinker, Albuquerque, NM;

Power of Attorney: The patent practitioners associated with Customer Number 020567.

Domestic Priority data as claimed by applicant

Foreign Applications

If Required, Foreign Filing License Granted: 05/26/2005

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US11/104,917**

Projected Publication Date: Request for Non-Publication Acknowledged

Non-Publication Request: Yes

Early Publication Request: No

Copy sent to DOE 6-20-05

Appendix B: Journal Articles about Superhydrophobic Coating

1. “Drying Transition of Confined Water,” *Nature*; vol. 442; August 3, 2006.

SUPERHYDROPHOBICITY

Drying transition of confined water

Long-range hydrophobic interactions operating underwater are important in the mediation of many natural and synthetic phenomena, such as protein folding, adhesion and colloid stability. Here we show that rough hydrophobic surfaces can experience attractive forces over distances more than 30 times greater than any reported previously, owing to the spontaneous evaporation of the intervening, confined water. Our finding highlights the importance of surface roughness in the interaction of extended structures in water, which has so far been largely overlooked.

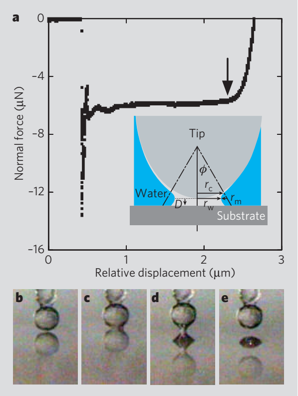


Figure 1 | Cavitation between superhydrophobic surfaces. a, Plot of force versus displacement for the underwater approach of a tip towards a flat surface. The experiment starts at zero micrometres relative displacement (arbitrarily defined). The sudden development of a negative (attractive) force at about 0.4 μm relative displacement corresponds to cavitation. Contact with the surface is indicated by the inflection at about 2.2 μm (arrow). The distance between the onset of adhesion and contact (1.8 μm) is the distance over which cavitation occurs for this sample. The inset shows the cavitation geometry: $\Delta p = \gamma(1/r_w - 1/r_m)$, where Δp is the pressure difference across the interface, γ is the liquid–vapour interfacial tension, r_m is the radius of the meniscus, r_w is the radius of its waist, and r_c is the contact radius of the cavity on the tip surface. D is the critical separation below which cavitation is thermodynamically favoured. See also supplementary information. **b–e**, Optical images of cavitation: **b**, position of superhydrophobic tip and substrate just before cavitation; **c**, cavitation occurs about 33 ms later; **d**, cavity meniscus, as seen during tip retraction, one frame before its unstable collapse; **e**, a cavity ‘bubble’ is left behind on both the tip and substrate. These bubbles, attributed to air supplied from water and the porous superhydrophobic surface, are unstable and are readsorbed in about 6 seconds. In all frames, the circular image at the bottom is the reflection of the spherical 150-μm-diameter tip in the flat superhydrophobic surface.

The existence of ‘long-range’ hydrophobic interactions has been debated for more than 25 years[1–5], because their reported range of 1–100 nanometres exceeds that of van der Waals forces and cannot be explained by water restructuring. However, investigations have been limited to smooth, flat model surfaces[4], even though most surfaces are rough. Roughness strongly influences wetting — as evidenced by the high water-contact angles ($\theta \geqslant 160°$) and rolling of water droplets on lotus leaves[6].

Knowing that superhydrophobic surfaces occur naturally and that living systems operate mainly in water, we investigated the interaction of rough superhydrophobic surfaces beneath the water surface. Interfacial-force microscopy[7] and optical imaging were used to examine the interaction between two approaching or retracting superhydrophobic surfaces (water contact angle θ of about 170°; see supplementary information) submerged in either air-equilibrated or de-aerated water.

We discovered a very-long-range hydrophobic interaction that was due to out-of-contact evaporation, or ‘cavitation’, of the intervening water at tip-to-substrate separations ranging from 0.8 μm to as much as 3.5 μm. Cavitation is a first-order phase transition characterized by a sudden, strong attractive force (Fig. 1a) and by the appearance of a vapour bridge spanning the tip-to-substrate gap (Fig. 1 b–e, and see supplementary information for details).

Pre-existing ‘nanobubbles’ of a size commensurate with the interaction length have been proposed as a source of long-range interactions[8]. We therefore used *in situ* confocal imaging to search for bubbles on an isolated, flat superhydrophobic surface (for details, see supplementary information). Neither the microscopy nor neutron reflectivity experiments[9] provide evidence for bubbles — certainly not micrometre-sized bubbles. We therefore argue that cavitation is a consequence of, and thermodynamically consistent with, the properties of confined water[10]. The critical separation, D, below which cavitation is thermodynamically favoured can be estimated from Laplace’s equation as 1.4 μm (see supplementary information): this is a lower bound and will increase if Δp, the pressure difference across the interface, is reduced by incorporation of air into the cavity.

Unambiguous cavitation has previously been observed only following the contact of smooth hydrophobic surfaces[3,8,11]. Although it is thermodynamically acceptable, out-of-contact cavitation has been modelled as having a large activation barrier[12], so we need to explain why we observe it and how kinetic barriers are surmounted.

First, we used interfacial-force microscopy[7], in which interfacial forces are counterbalanced, to avoid snap-to-contact (when the rate of change of the force exceeds the spring constant and the two surfaces snap together uncontrollably, as occurs in atomic-force microscopy and in surface-force apparatus studies[5]). Second, the calculated D for submerged superhydrophobic surfaces is more than ten times that of smooth surfaces, which increases the probability of cavity nucleation at larger separations. Third, the submerged superhydrophobic surface presents an intrinsic liquid/vapour/solid interface, which may serve as a heterogeneous nucleation surface.

We simulated the molecular dynamics of a model fluid, which showed the necessary liquid–vapour behaviour, confined between two closely spaced surfaces containing opposing ($\theta = 180°$) superhydrophobic patches. The simulations show that cavitation occurs by the growth of capillary-like fluctuations of vapour films extending from the superhydrophobic surfaces, leading to the sudden formation and growth of a vapour bridge.

Our experiments reveal that cavitation can be one source of long-range hydrophobic interactions. For rough surfaces, the interaction length extends to micrometre scales. Correspondingly, interaction lengths of hundreds of nanometres, observed for smooth surfaces (for example, snap-to-contact), might also be explained by cavitation, in agreement with thermodynamic expectations.

Seema Singh*, Jack Houston*, Frank van Swol*†, C. Jeffrey Brinker*†
*Sandia National Laboratories, PO Box 5800, Albuquerque, New Mexico 87185, USA
e-mail: cjbrink@sandia.gov
†University of New Mexico, Albuquerque, New Mexico 87131, USA

1. Blake, T. D. & Kitchener J. A. *J. Chem. Soc. Farad. Trans. 1* **68,** 1435–1442 (1972).
2. Christenson, H. K. & Claesson, P. M. *Adv. Colloid Interface Sci.* **91,** 391–436 (2001).
3. Christenson, H. K. & Claesson, P. M. *Science* **239,** 390–392 (1988).
4. Israelachvili, J. & Pashley, R. *Nature* **300,** 341–342 (1982).
5. Stevens, H., Considine, R. F., Drummond, C. J., Hayes, R. A. & Attard, P. *Langmuir* **21,** 6399–6405 (2005).
6. Lafuma, A. & Quéré, D. *Nature Mater.* **2,** 457–460 (2003).
7. Joyce, S. A. & Houston, J. E. *Rev. Sci. Instr.* **62,** 710–715 (1991).
8. Parker, J. L., Claesson, P. M. & Attard, P. *J. Phys. Chem.* **98,** 8468–8480 (1994).
9. Doshi, D. *et al. Langmuir* **21,** 7805–7811 (2005).
10. Lum, K., Chandler, D. & Weeks, J. D. *J. Phys. Chem. B* **103,** 4570-4577 (1999).
11. Pashley, R. M., McGuiggan, P. M., Ninham, B.W. & Evans, F. D. *Science* **229,** 1088–1089 (1985).
12. Luzar, A. *J. Phys. Chem. B* **108,** 19859–19866 (2004).

Supplementary information accompanies this communication on *Nature*’s website.
Received 15 December 2005; accepted 15 June 2006.
Competing financial interests: declared none.
doi:10.1038/442526a

BRIEF COMMUNICATIONS ARISING online
www.nature.com/bca see *Nature* contents.

2. "Investigating the Interface of Superhydrophobic Surfaces in Contact with Water," Dhaval A. Doshi, Pratik B. Shah, Seema Singh, Eric D. Branson, Anthony P. Malanoski, Erik B. Watkins, Jaroslaw Majewski, Frank van Swol, and C. Jeffrey Brinker; *Langmuir*; 2005; no 21; p. 7805-7811.

EXCERPT

Langmuir **2005,** *21,* 7805−7811 7805

Investigating the Interface of Superhydrophobic Surfaces in Contact with Water

Dhaval A. Doshi,*[†,⊥] Pratik B. Shah,[‡] Seema Singh,[‡] Eric D. Branson,[‡]
Anthony P. Malanoski,[‡,||] Erik B. Watkins,[†] Jaroslaw Majewski,[†]
Frank van Swol,[‡,§] and C. Jeffrey Brinker[‡,§]

*Lujan Neutron Scattering Center, Los Alamos National Laboratory,
Los Alamos, New Mexico 87545, Center for Micro-Engineered Materials,
University of New Mexico, Albuquerque, New Mexico 87106, and
Sandia National Laboratories, Albuquerque, New Mexico 87106*

Received March 21, 2005. In Final Form: June 11, 2005

Neutron reflectivity (NR) is used to probe the solid, liquid, vapor interface of a porous superhydrophobic (SH) surface submerged in water. A low-temperature, low-pressure technique was used to prepare a rough, highly porous organosilica aerogel-like film. UV/ozone treatments were used to control the surface coverage of hydrophobic organic ligands on the silica framework, allowing the contact angle with water to be continuously varied over the range of 160° (superhydrophobic) to <10° (hydrophilic). NR shows that the superhydrophobic nature of the surface prevents infiltration of water into the porous film. Atomic force microscopy and density functional theory simulations are used in combination to interpret the NR results and help establish the location, width, and nature of the SH film−water interface.

Introduction

We all can recall seeing water droplets "bead up" on the leaves of plants. Most famous is the Lotus leaf, called the "symbol of purity" because of its self-cleaning properties. At very shallow angles of inclination or with the slightest wind, water droplets roll rather than flow.[1,2] The rolling droplets entrain particle contaminants and parasites, thereby cleaning them from the Lotus leaf surface. It is now recognized that the fascinating fluid behaviors observed for the Lotus plant, like the rolling and bouncing of liquid droplets and self-cleaning of particle contaminants, arise from a combination of the low interfacial energy and the rough surface topography of waxy deposits covering their leaves.[3]

Phenomenologically, Cassie and Baxter postulated that the cosine of the contact angle on a heterogeneous solid/air surface is the sum of the cosine of the contact angles of the respective homogeneous surfaces weighted by the surface fraction of the solid,[4,5] $\cos\theta^{\propto} = -1 + \Phi_s(1 + \cos\theta)$, where $\theta^{\propto}$ is the apparent contact angle, −1 is the cosine of the contact angle of the air surface, and Φ_s is the surface fraction of solid. As the ratio of the pillar width to interpillar distance of a regular lithographically defined surface decreases[6] or the roughness of a random, porous (e.g., fractal) surface increases, Φ_s approaches zero, and $\theta^{\propto}$ approaches 180°. Interestingly, Herminghaus postulates that hierarchical roughness could render any surface (independent of microscopic contact angle) superhydrophobic,[7] but this has not yet been observed. Wenzel had put forward a different relationship for contact angles on rough surfaces:[8] $\cos\theta^{\propto} = r\cos\theta$, where r is the roughness parameter defined by the ratio of the real surface area to the projected surface area. Because $r \geq 1$, roughness on a hydrophobic surface ($\theta > 90°$) renders it more hydrophobic, whereas on a hydrophilic surface ($\theta < 90°$) roughness has the opposite effect, decreasing θ toward 0°. Although the Wenzel equation is valid when the liquid droplet enters the valleys and completely wets the surface topography, the Cassie−Baxter model requires the presence of a liquid−vapor interface below the droplet.[9] At constant surface roughness, the surface chemistry can be designed to have the contact-angle behavior go from the Wenzel regime to the Cassie−Baxter regime.

Devising synthetic methods to produce superhydrophobic (SH) surfaces is the subject of intensive, ongoing, worldwide research.[10−32] SH properties such as self-

---

[†] Los Alamos National Laboratory.

[‡] University of New Mexico.

[§] Sandia National Laboratories.

[||] Currently at the Naval Research Laboratory.

[⊥] Currently at Cabot Corporation, MA 01821.

(1) Barthlott, W.; Neinhuis, C. *Planta (Heidelberg)* **1997**, *202*, 1.

(2) Neinhuis, C.; Barthlott, W. *Ann. Bot. (London)* **1997**, *79*, 667.

(3) Koch, K.; Neinhuis, C.; Ensikat, H. J.; Barthlott, W. *J. Exp. Bot.* **2004**, *55*, 711.

(4) Cassie, A. B. D. *Discuss. Faraday Soc.* **1948**, *3*, 11.

(5) Cassie, A. B. D.; Baxter, S. *Trans. Faraday Soc.* **1944**, *40*, 546.

(6) He, B.; Patankar, N. A.; Lee, J. *Langmuir* **2003**, *19*, 4999.

(7) Herminghaus, S. *Europhys. Lett.* **2000**, *52*, 165.

(8) Wenzel, R. N. *Ind. Eng. Chem.* **1936**, *28*, 988.

(9) Bico, J.; Marzolin, C.; Quere, D. *Europhys. Lett.* **1999**, *47*, 220.

(10) Chen, A. C.; Peng, X. S.; Koczkur, K.; Miller, B. *Chem. Commun.* **2004**, 1964.

(11) Favia, P.; Cicala, G.; Milella, A.; Palumbo, F.; Rossini, R.; d'Agostino, R. *Surf. Coat. Technol.* **2003**, *169/170*, 609.

(12) Feng, L.; Li, S. H.; Li, Y. S.; Li, H. J.; Zhang, L. J.; Zhai, J.; Song, Y. L.; Liu, B. Q.; Jiang, L.; Zhu, D. B. *Adv. Mater.* **2002**, *14*, 1857.

(13) Flemming, M.; Hultaker, A.; Reihs, K.; Duparre, A. *Proc. Soc. Photo-Opt. Instrum. Eng.* **2003**, *5250*, 56.

(14) Khorasani, M. T.; Mirzadeh, H.; Sammes, P. G. *Radiat. Phys. Chem.* **1996**, *47*, 881.

(15) Klein, R. J.; Biesheuvel, R. M.; Yu, B. C.; Meinhart, C. D.; Lange, F. F. *Z. Metallkd.* **2003**, *94*, 377.

(16) Nakajima, A.; Abe, K.; Hashimoto, K.; Watanabe, T. *Thin Solid Films* **2000**, *376*, 140.

(17) Ren, S. L.; Yang, S. R.; Zhao, Y. *Acta Mech. Sinica* **2004**, *20*, 159.

(18) Sasaki, M.; Kieda, N.; Katayama, K.; Takeda, K.; Nakajima, A. *J. Mater. Sci.* **2004**, *39*, 3717.

(19) Shirtcliffe, N. J.; Sanaa, A.; Evans, C.; McHale, G.; Newton, M. I.; Perry, C. C.; Roach, P. *J. Micromech. Microeng.* **2004**, *14*, 1384.

(20) Teare, D. O. H.; Spanos, C. G.; Ridley, P.; Kinmond, E. J.; Roucoules, V.; Badyal, J. P. S.; Brewer, S. A.; Coulson, S.; Willis, C. *Chem. Mater.* **2002**, *14*, 4566.

(21) Woodward, I.; Schofield, W. C. E.; Roucoules, V.; Badyal, J. P. S. *Langmuir* **2003**, *19*, 3432.

(22) Feng, L.; Li, S. H.; Li, H. J.; Zhai, J.; Song, Y. L.; Jiang, L.; Zhu, D. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 1221.

(23) Zhang, X.; Shi, F.; Yu, X.; Liu, H.; Fu, Y.; Wang, Z. Q.; Jiang, L.; Li, X. Y. *J. Am. Chem. Soc.* **2004**, *126*), 3064.

(24) Shin, J. Y.; Kuo, C. W.; Chen, P. L.; Mon, C. Y. *Mater. Res. Soc. Symp. Proc.* **2004**, *823*, 181.

(25) Shirtcliffe, N. J.; McHale, G.; Newton, M. I.; Chabrol, G.; Perry, C. C. *Adv. Mater.* **2004**, *16*, 1929.

10.1021/la050750s CCC: $30.25

3. "Effective Slip on Textured Superhydrophobic Surfaces," Salil Gogte, Peter Vorobieff, Richard Truesdell, Andrea Mammoli, Frank van Swol, Pratik Shah, and C. Jeffrey Brinker; *Physics of Fluids*; 2005; no. 17.

EXCERPT

HTML ABSTRACT + LINKS

PHYSICS OF FLUIDS **17**, 051701 (2005)

Effective slip on textured superhydrophobic surfaces

Salil Gogte, Peter Vorobieff, Richard Truesdell, and Andrea Mammoli
The University of New Mexico, Albuquerque, New Mexico 87131

Frank van Swol
The University of New Mexico, Albuquerque, New Mexico 87131
and Sandia National Laboratories, Albuquerque, New Mexico 87185

Pratik Shah
The University of New Mexico, Albuquerque, New Mexico 87131

C. Jeffrey Brinker
The University of New Mexico, Albuquerque, New Mexico 87131
and Sandia National Laboratories, Albuquerque, New Mexico 87185

(Received 19 November 2004; accepted 28 February 2005; published online 13 April 2005)

We study fluid flow in the vicinity of textured and superhydrophobically coated surfaces with characteristic texture sizes on the order of 10 μm. Both for droplets moving down an inclined surface and for an external flow near the surface (hydrofoil), there is evidence of appreciable drag reduction in the presence of surface texture combined with superhydrophobic coating. On textured inclined surfaces, the drops roll faster than on a coated untextured surface at the same angle. The highest drop velocities are achieved on surfaces with irregular textures with characteristic feature size $\sim$8 μm. Application of the same texture and coating to the surface of a hydrofoil in a water tunnel results in drag reduction on the order of 10% or higher. This behavior is explained by the reduction of the contact area between the surface and the fluid, which can be interpreted in terms of changing the macroscopic boundary condition to allow nonzero slip velocity. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1896405]

An interface between a viscous fluid and a solid surface is usually characterized by a no-slip boundary condition, although the notion of possible slip on the boundary was introduced almost 200 years ago.[1] Slip on the boundary can occur on the scale on the order of tens of nanometers,[2–4] but the effects of this phenomenon are not appreciable for macroscopic flows. In countless applications, a limited slip boundary condition would be highly desirable. The motivations include, but are not limited to, drag and pressure drop reduction. Recent advances in materials science have led to creation of superhydrophobic (SH) surfaces with unusual contact properties and motivated new research on the boundary conditions near the latter,[5] although apparently there is no macroscopic slip near SH surfaces produced by application of SH coating to a smooth substrate.

The defining property of SH surfaces is a very high contact angle θ, measured as the angle between the plane of the surface and the tangent to the surface of a droplet resting on it: $\theta > 140°$ [Fig. 1(a)]. We show that in fluid flow near a textured SH surface (e.g., a drop moving down an incline), due to this high θ, the contact area between the fluid and the surface is reduced, producing effective macroscopic slip on scales consistent with the characteristic size of the surface features.

Our basic notion of the flow behavior near a textured SH surface is illustrated in Fig. 1. The characteristic size of the texture is much larger than any surface roughness associated with the SH coating itself, but smaller than the capillary length (2.7 mm for water). The texture can be regular (e.g., grooves) or irregular (random peaks). The direct contact area between the surface and the fluid is limited to the protruding parts of the surface (lands for the regular texture, peaks for the irregular texture), with free fluid surface areas above the depressed parts (grooves for the regular texture, valleys for the irregular texture). We assume that these areas exist because there is insufficient energy to deform the fluid boundary to bring it in contact with all the surface [Fig. 1(a)]. This will lead to a velocity profile in the plane of the lands with zero velocity in the contact area and nearly parabolic velocity distribution in the grooves. A velocity average at the nominal fluid boundary (the plane of the lands) would be greater than zero [Fig. 1(b)]. Similar behavior can be expected for an irregular texture [Fig. 1(c)], although the shape of the real-life boundary of the fluid in the latter case is likely more complicated.

For a flow inside a round pipe with alternating slip/no-slip boundary condition, an analytical solution manifests nontrivial effective slip velocity.[6] For a fixed ratio between the widths of the lands and the grooves, this solution predicts effective slip to increase linearly with the land width. To visualize a plausible velocity distribution near a surface in partial contact with fluid, we conducted a simple finite-element numerical simulation of a Poiseuille flow in a circular cross-section tube with alternating boundary conditions (Fig. 2) for a 1:1 ratio between the widths of the lands (no slip) and the grooves (slip). The simulation shows effective slip increasing with the land width linearly in good agreement with the analytical results.[6] Thus one should expect

1070-6631/2005/17(5)/051701/4/$22.50

Appendix B: Journal Articles about Superhydrophobic Coating

4. “Characterization of Superhydrophobic Materials Using Multiresonance Acoustic Shear Wave Sensors,” Sun Jong Kwoun, Ryszard M. Lec, Richard A. Cairncross, Pratik Shah, and C. Jeffrey Brinker; *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control*; vol. 53, no. 8; August 2006.

EXCERPT

Letters

Characterization of Superhydrophobic Materials Using Multiresonance Acoustic Shear Wave Sensors

Sun Jong Kwoun, Ryszard M. Lec, Richard A. Cairncross, Pratik Shah, and C. Jeffrey Brinker

***Abstract*—Various superhydrophobic (SH) surfaces, with enhanced superhydrophobicity achieved by the use of nanoparticles, were characterized by a new acoustic sensing technique using multiresonance thickness-shear mode (MTSM) sensors. The MTSM sensors were capable of differentiating SH properties created by nano-scale surface features for film, exhibiting similar macroscopic contact angles.**

I. Introduction

In recent years, a variety of synthetic approaches have been developed to create so-called superhydrophobic (SH) surfaces characterized normally by high static contact angles of water ($> 150°$) [1]–[4]. Superhydrophobicity depends on surface roughness and surface chemistry, but to date rigorous structure-property relationships have not been established, especially the relationship between static and dynamic properties and how superhydrophobicity is influenced by nanoscale structural features. In this paper we use high-frequency shear acoustic waves generated by a piezoelectric quartz resonator thickness-shear mode (TSM) sensor to interrogate SH surfaces loaded with liquid media. For the TSM operating in the frequency range of 1 to ~100 MHz, the depth of penetration is on the order of tens to thousands of nanometers [5]; therefore, these sensors are sensitive to nanoscale interfacial phenomena and processes. Moreover, because the depth of penetration decreases with increasing TSM frequency, a multiresonance excitation of the sensor allows spatial interrogation of the interface with controllable interrogation depth. The purpose of this investigation is to evaluate the multiresonance TSM sensing technique to study the dynamic behavior of the SH/H_2O interface and to correlate the multiresonance TSM (MTSM) response with microscopic and nanoscopic features of SH surfaces. Although all the SH surfaces in this study had similar macroscopic wettability (optical contact angle ~150°), MTSM showed different responses, depending on the surface treatments and film morphology. Thus, MTSM sensing may provide a new means of probing the functional behavior of SH films and help establish needed structure-property relationships.

II. Experiment

The TSM sensors were 10 MHz fundamental resonant frequency quartz crystals AT-cut and coated initially with gold electrodes on both sides. Five samples of varying hydrophobicity were prepared by coating the sensors and subjecting the coating to various surface treatments (Table I summarizes the sample preparation). Sample 1 was a bare TSM sensor and Samples 2 to 4A were coated with SH coatings of increasing hydrophobicity. Sample 2 was coated with TFPTMOS (trifluoropropyltrimethoxysilane) to produce a low-surface, free energy with submicron-scale roughness [4]. Sample 3 also had a TFPTMOS coating but was further treated with HMDS (hexamethyldisilizane) to derivatize any remaining hydroxyl groups with hydrophobic trimethyl silyl $Si(CH_3)_3$ groups on the surface. Sample 4A was prepared by the same techniques as Sample 3 but with the addition of silica nanoparticles (2% by weight) to the TFPTMOS coating, followed by treatment with HMDS. Sample 4B is the same MTSM sensor and coating as Sample 4A but after exposure to ultraviolet (UV)/ozone to reduce its hydrophobicity. All the SH samples were prepared in the laboratory at the University of New Mexico.

The samples were characterized for macroscopic contact angle and surface roughness. Contact angle was measured by the sessile drop method [6]. The surface topology and roughness of samples was measured using atomic force microscopy (AFM) [7]. The AFM images of the SH surfaces were obtained in 3 μm × 3 μm areas and are shown in Fig. 1. The AFM software enables analysis of relative changes of surface area (Table I).

III. Results and Discussion

The measured macroscopic optical contact angles of water on each of the samples are reported in Table I along with images of a water droplet resting on the sample surface. The contact angle increases from approximately 80° on the bare MTSM sensor to 140° to 155° for the SH coatings; Ultraviolet/ozone treatment reduces the contact angle to approximately 90° by changing the surface energy without affecting morphology. Samples 2, 3, and 4A are all SH with contact angles of 140° or more. The addition of silica nanoparticles in Sample 4A does not significantly increase the contact angle compared to Sample 3.

The surface area of the samples, as measured by AFM (Fig. 1), increases steadily from Sample 1 to 4A. The surface area of Sample 4A was approximately 46% larger than the initial surface area because of roughness resulting from the surface treatment. Samples 3 and 4A had similar surface areas and exhibited high contact angles characteristic of SH surfaces. So according to standard static characterization protocols, both Samples 3 and 4 were equally SH.

Manuscript received January 10, 2006; accepted February 16, 2006.

S. J. Kwoun, R. M. Lec, and R. A. Cairncross are with Drexel University, Philadelphia, PA 19104 (e-mail: sunkwoun@gmail.com).

P. Shah and C. J. Brinker are with the University of New Mexico, Albuquerque, NM 87131.

0885–3010/$20.00 © 2006 IEEE

5. “Drag Reduction on a Patterned Superhydrophobic Surface,” Richard Truesdell, Andrea Mammoli, Peter Vorobieff, Frank van Swol, and C. Jeffrey Brinker; *Physical Review Letters*; July 28, 2006.

EXCERPT

PRL **97,** 044504 (2006) PHYSICAL REVIEW LETTERS week ending 28 JULY 2006

Drag Reduction on a Patterned Superhydrophobic Surface

Richard Truesdell,[1] Andrea Mammoli,[1] Peter Vorobieff,[1] Frank van Swol,[1,2] and C. Jeffrey Brinker[1,2]
[1] *Department of Mechanical Engineering, The University of New Mexico, Albuquerque, New Mexico 87131, USA*
[2] *Sandia National Laboratories, Albuquerque, New Mexico 87185, USA*

(Received 3 May 2006; published 26 July 2006)

We present an experimental study of a low-Reynolds number shear flow between two surfaces, one of which has a regular grooved texture augmented with a superhydrophobic coating. The combination reduces the effective fluid-surface contact area, thereby appreciably decreasing the drag on the surface and effectively changing the *macroscopic* boundary condition on the surface from no slip to limited slip. We measure the force on the surface and the velocity field in the immediate vicinity on the surface (and thus the wall shear) simultaneously. The latter facilitates a direct assessment of the effective slip length associated with the drag reduction.

DOI: 10.1103/PhysRevLett.97.044504 PACS numbers: 47.45.Gx, 47.61.−k, 47.85.lb

On the boundary between a viscous fluid and a solid surface the fluid velocity with respect to the surface is generally assumed to be zero (no-slip condition), and the amount of experience verifying this assumption is massive. From molecular dynamics considerations, while slip may occur on the boundary, its effects should be confined to the nanoscale realm. This notion is also well supported by experimental results [1,2]. Thus it is inevitable that in any fluid flow, one has to deal with shear caused by the difference between the free-stream velocity and the zero boundary velocity. This shear is the reason for the drag force on any body moving through fluid and for the pressure drop in any internal flow. The practical motivation to reduce the drag and the pressure drop is great, but is there anything that *can* be done?

In turbulent flows, a large fraction of the drag is produced by intermittent coherent structures. The energy dissipation by these structures can be reduced [3,4] by smoothing (laminarizing) the flow field. The next question that arises is if the *laminar* drag can be decreased without changing the macroscopic flow parameters (free-stream fluid properties, body size, geometry and surface temperature, etc.). Recent works [5–7] report evidence of such drag decrease obtained by reducing the effective contact area between the solid and the fluid. The fundamental importance of such flows over soft or patterned surfaces has been recently emphasized [8].

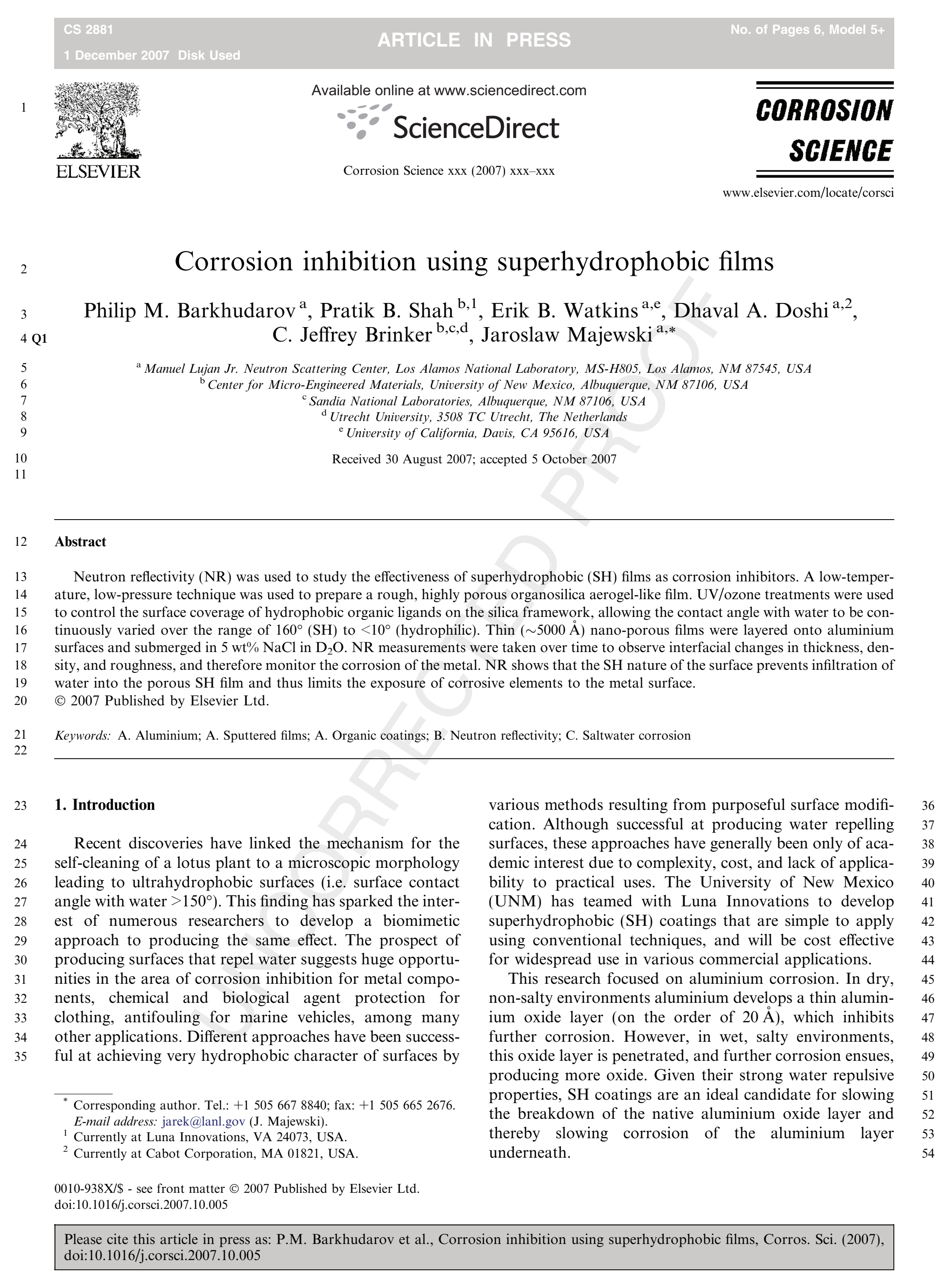
The contact area minimization was made possible by the development of superhydrophobic (SH) coatings. These coatings greatly decrease the energy of the interaction between the surface and the fluid, leading to unusually high contact angles for drops resting on SH surfaces [9]. If the solid surface is textured, with a regular or irregular pattern, a regime may emerge where there is insufficient energy to deform the fluid interface to bring it in contact with the entire solid surface [Cassie regime [9]], resulting in voids forming in the recessed parts of the pattern. For the parts of the fluid interface above the voids, the no-slip boundary condition will be no longer applicable, and the simplest boundary-condition assumption for these parts will be free slip (no shear on the interface), although in reality there still may be some small drag transmitted to the no-contact patches by the gas filling the voids. For a regular pattern of recessed grooves (free-slip) and protruding lands (no-slip), both analytical [10] and numerical [7,10] solutions show the drag to decrease with the characteristic size of the recessed surface features. As the feature size becomes larger, however, the fluid once again will come into contact with the recessed parts of the pattern, thus limiting the scale range of surface features that result in sliplike behavior.

While the feature sizes characteristic of the SH coating itself are usually on a submicron scale, voids can be greatly increased in size if the SH coating is applied to a textured surface [6,7] with features on the scale from microns to tens of microns, thereby producing a measurable change in the pressure drop [6] in an internal flow, in the terminal velocity of a drop rolling down the surface [7], or in the drag coefficient in an external flow [7]. It has been stipulated that, while there is no slip on the microscopic scale, the *macroscopic* boundary condition for the tangential velocity component u near a textured SH surface can be interpreted as Navier slip [11], with the slip velocity at the wall u_s proportional to the shear: $u_s = b(\partial u/\partial y)$. The direction y is normal to the wall, and the dimensional coefficient b is the *slip length*.

In this Letter, we present flow measurements near a regularly textured SH surface in shear flow showing *macroscopic* effective [12] [or apparent [8,12]] slip leading to drag reduction on the order of 20%. Moreover, the observed results cannot be entirely explained by the reduction of drag due solely to the formation of slip areas above the grooves in the pattern, suggesting that additional dynamic effects [e.g., related to nanobubble formation [13]] may play a role, as discussed below. In our experiment, reliable optical measurements are taken simultaneously with torque measurements. With the former, we measure the velocity field and extract the liquid-solid interface stress. The latter provide a direct measurement of the stress. Knowing the difference between the actual measured stress

6. “Corrosion Inhibition Using Superhyrdrophobic Films,” Philip M. Barkhudarov, Pratik B. Shah, Erik B. Watkins, Dhaval A. Doshi, C. Jeffrey Brinkerb, and Jaroslaw Majewski, *Corrosion Science*. (In Submission)

EXCERPT



CS 2881
1 December 2007 Disk Used
ARTICLE IN PRESS
No. of Pages 6, Model 5+

ELSEVIER
Available online at www.sciencedirect.com
ScienceDirect
Corrosion Science xxx (2007) xxx–xxx
CORROSION SCIENCE
www.elsevier.com/locate/corsci

Corrosion inhibition using superhydrophobic films

Philip M. Barkhudarov [a], Pratik B. Shah [b,1], Erik B. Watkins [a,e], Dhaval A. Doshi [a,2], C. Jeffrey Brinker [b,c,d], Jaroslaw Majewski [a,*]

[a] *Manuel Lujan Jr. Neutron Scattering Center, Los Alamos National Laboratory, MS-H805, Los Alamos, NM 87545, USA*
[b] *Center for Micro-Engineered Materials, University of New Mexico, Albuquerque, NM 87106, USA*
[c] *Sandia National Laboratories, Albuquerque, NM 87106, USA*
[d] *Utrecht University, 3508 TC Utrecht, The Netherlands*
[e] *University of California, Davis, CA 95616, USA*

Received 30 August 2007; accepted 5 October 2007

Abstract

Neutron reflectivity (NR) was used to study the effectiveness of superhydrophobic (SH) films as corrosion inhibitors. A low-temperature, low-pressure technique was used to prepare a rough, highly porous organosilica aerogel-like film. UV/ozone treatments were used to control the surface coverage of hydrophobic organic ligands on the silica framework, allowing the contact angle with water to be continuously varied over the range of 160° (SH) to <10° (hydrophilic). Thin (~5000 Å) nano-porous films were layered onto aluminium surfaces and submerged in 5 wt% NaCl in D_2O. NR measurements were taken over time to observe interfacial changes in thickness, density, and roughness, and therefore monitor the corrosion of the metal. NR shows that the SH nature of the surface prevents infiltration of water into the porous SH film and thus limits the exposure of corrosive elements to the metal surface.

Keywords: A. Aluminium; A. Sputtered films; A. Organic coatings; B. Neutron reflectivity; C. Saltwater corrosion

1. Introduction

Recent discoveries have linked the mechanism for the self-cleaning of a lotus plant to a microscopic morphology leading to ultrahydrophobic surfaces (i.e. surface contact angle with water >150°). This finding has sparked the interest of numerous researchers to develop a biomimetic approach to producing the same effect. The prospect of producing surfaces that repel water suggests huge opportunities in the area of corrosion inhibition for metal components, chemical and biological agent protection for clothing, antifouling for marine vehicles, among many other applications. Different approaches have been successful at achieving very hydrophobic character of surfaces by various methods resulting from purposeful surface modification. Although successful at producing water repelling surfaces, these approaches have generally been only of academic interest due to complexity, cost, and lack of applicability to practical uses. The University of New Mexico (UNM) has teamed with Luna Innovations to develop superhydrophobic (SH) coatings that are simple to apply using conventional techniques, and will be cost effective for widespread use in various commercial applications.

This research focused on aluminium corrosion. In dry, non-salty environments aluminium develops a thin aluminium oxide layer (on the order of 20 Å), which inhibits further corrosion. However, in wet, salty environments, this oxide layer is penetrated, and further corrosion ensues, producing more oxide. Given their strong water repulsive properties, SH coatings are an ideal candidate for slowing the breakdown of the native aluminium oxide layer and thereby slowing corrosion of the aluminium layer underneath.

---

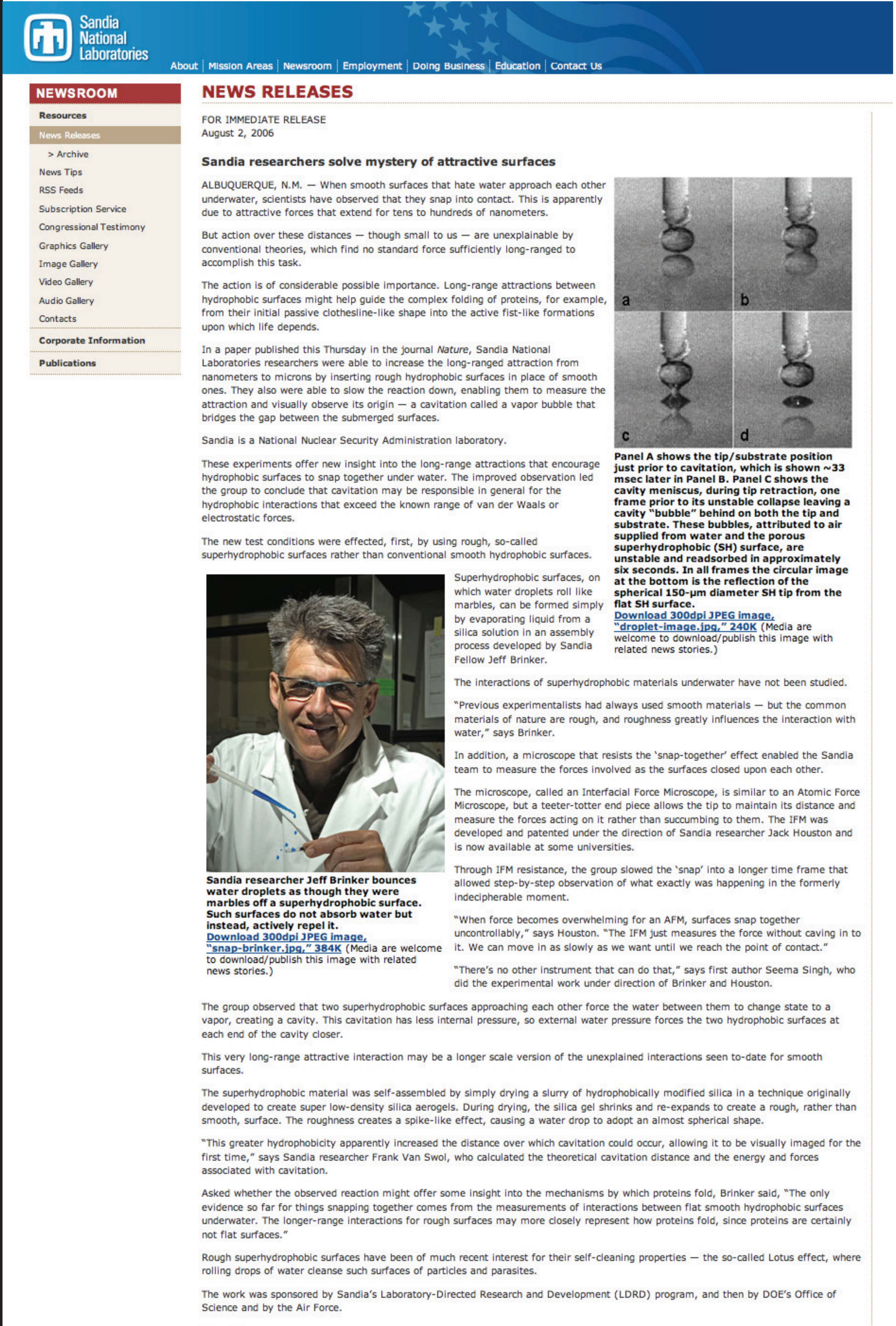
[*] Corresponding author. Tel.: +1 505 667 8840; fax: +1 505 665 2676.
E-mail address: jarek@lanl.gov (J. Majewski).
[1] Currently at Luna Innovations, VA 24073, USA.
[2] Currently at Cabot Corporation, MA 01821, USA.

0010-938X/$ - see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.corsci.2007.10.005

Please cite this article in press as: P.M. Barkhudarov et al., Corrosion inhibition using superhydrophobic films, Corros. Sci. (2007), doi:10.1016/j.corsci.2007.10.005

Appendix C: News and Magazine Articles about Superhydrophobic Coating

1. "Sandia Researchers Solve Mystery of Attractive Surfaces," *Sandia Lab News*; August 2, 2006.



NEWS RELEASES

FOR IMMEDIATE RELEASE
August 2, 2006

Sandia researchers solve mystery of attractive surfaces

ALBUQUERQUE, N.M. — When smooth surfaces that hate water approach each other underwater, scientists have observed that they snap into contact. This is apparently due to attractive forces that extend for tens to hundreds of nanometers.

But action over these distances — though small to us — are unexplainable by conventional theories, which find no standard force sufficiently long-ranged to accomplish this task.

The action is of considerable possible importance. Long-range attractions between hydrophobic surfaces might help guide the complex folding of proteins, for example, from their initial passive clothesline-like shape into the active fist-like formations upon which life depends.

In a paper published this Thursday in the journal *Nature*, Sandia National Laboratories researchers were able to increase the long-ranged attraction from nanometers to microns by inserting rough hydrophobic surfaces in place of smooth ones. They also were able to slow the reaction down, enabling them to measure the attraction and visually observe its origin — a cavitation called a vapor bubble that bridges the gap between the submerged surfaces.

Sandia is a National Nuclear Security Administration laboratory.

These experiments offer new insight into the long-range attractions that encourage hydrophobic surfaces to snap together under water. The improved observation led the group to conclude that cavitation may be responsible in general for the hydrophobic interactions that exceed the known range of van der Waals or electrostatic forces.

The new test conditions were effected, first, by using rough, so-called superhydrophobic surfaces rather than conventional smooth hydrophobic surfaces.

Panel A shows the tip/substrate position just prior to cavitation, which is shown ~33 msec later in Panel B. Panel C shows the cavity meniscus, during tip retraction, one frame prior to its unstable collapse leaving a cavity "bubble" behind on both the tip and substrate. These bubbles, attributed to air supplied from water and the porous superhydrophobic (SH) surface, are unstable and readsorbed in approximately six seconds. In all frames the circular image at the bottom is the reflection of the spherical 150-μm diameter SH tip from the flat SH surface.
Download 300dpi JPEG image, "droplet-image.jpg," 240K (Media are welcome to download/publish this image with related news stories.)

Sandia researcher Jeff Brinker bounces water droplets as though they were marbles off a superhydrophobic surface. Such surfaces do not absorb water but instead, actively repel it.
Download 300dpi JPEG image, "snap-brinker.jpg," 384K (Media are welcome to download/publish this image with related news stories.)

Superhydrophobic surfaces, on which water droplets roll like marbles, can be formed simply by evaporating liquid from a silica solution in an assembly process developed by Sandia Fellow Jeff Brinker.

The interactions of superhydrophobic materials underwater have not been studied.

"Previous experimentalists had always used smooth materials — but the common materials of nature are rough, and roughness greatly influences the interaction with water," says Brinker.

In addition, a microscope that resists the 'snap-together' effect enabled the Sandia team to measure the forces involved as the surfaces closed upon each other.

The microscope, called an Interfacial Force Microscope, is similar to an Atomic Force Microscope, but a teeter-totter end piece allows the tip to maintain its distance and measure the forces acting on it rather than succumbing to them. The IFM was developed and patented under the direction of Sandia researcher Jack Houston and is now available at some universities.

Through IFM resistance, the group slowed the 'snap' into a longer time frame that allowed step-by-step observation of what exactly was happening in the formerly indecipherable moment.

"When force becomes overwhelming for an AFM, surfaces snap together uncontrollably," says Houston. "The IFM just measures the force without caving in to it. We can move in as slowly as we want until we reach the point of contact."

"There's no other instrument that can do that," says first author Seema Singh, who did the experimental work under direction of Brinker and Houston.

The group observed that two superhydrophobic surfaces approaching each other force the water between them to change state to a vapor, creating a cavity. This cavitation has less internal pressure, so external water pressure forces the two hydrophobic surfaces at each end of the cavity closer.

This very long-range attractive interaction may be a longer scale version of the unexplained interactions seen to-date for smooth surfaces.

The superhydrophobic material was self-assembled by simply drying a slurry of hydrophobically modified silica in a technique originally developed to create super low-density silica aerogels. During drying, the silica gel shrinks and re-expands to create a rough, rather than smooth, surface. The roughness creates a spike-like effect, causing a water drop to adopt an almost spherical shape.

"This greater hydrophobicity apparently increased the distance over which cavitation could occur, allowing it to be visually imaged for the first time," says Sandia researcher Frank Van Swol, who calculated the theoretical cavitation distance and the energy and forces associated with cavitation.

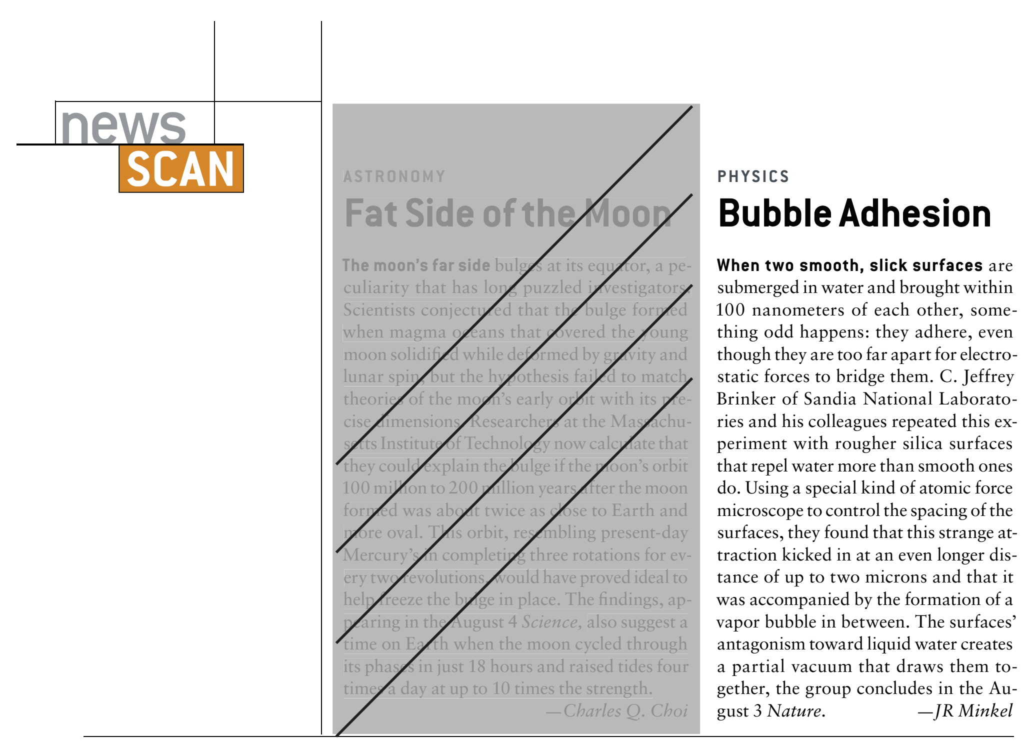
Asked whether the observed reaction might offer some insight into the mechanisms by which proteins fold, Brinker said, "The only evidence so far for things snapping together comes from the measurements of interactions between flat smooth hydrophobic surfaces underwater. The longer-range interactions for rough surfaces may more closely represent how proteins fold, since proteins are certainly not flat surfaces."

Rough superhydrophobic surfaces have been of much recent interest for their self-cleaning properties — the so-called Lotus effect, where rolling drops of water cleanse such surfaces of particles and parasites.

The work was sponsored by Sandia's Laboratory-Directed Research and Development (LDRD) program, and then by DOE's Office of Science and by the Air Force.

Appendix C: News and Magazine Articles about Superhydrophobic Coating

2. “Bubble Adhesion,” *Scientific America*; vol. 295, issue 4; October 2006.



news SCAN

~~ASTRONOMY~~

~~Fat Side of the Moon~~

~~**The moon’s far side** bulges at its equator, a peculiarity that has long puzzled investigators. Scientists conjectured that the bulge formed when magma oceans that covered the young moon solidified while deformed by gravity and lunar spin, but the hypothesis failed to match theories of the moon’s early orbit with its precise dimensions. Researchers at the Massachusetts Institute of Technology now calculate that they could explain the bulge if the moon’s orbit 100 million to 200 million years after the moon formed was about twice as close to Earth and more oval. This orbit, resembling present-day Mercury’s in completing three rotations for every two revolutions, would have proved ideal to help freeze the bulge in place. The findings, appearing in the August 4 *Science*, also suggest a time on Earth when the moon cycled through its phases in just 18 hours and raised tides four times a day at up to 10 times the strength.~~

~~*—Charles Q. Choi*~~

PHYSICS

Bubble Adhesion

When two smooth, slick surfaces are submerged in water and brought within 100 nanometers of each other, something odd happens: they adhere, even though they are too far apart for electrostatic forces to bridge them. C. Jeffrey Brinker of Sandia National Laboratories and his colleagues repeated this experiment with rougher silica surfaces that repel water more than smooth ones do. Using a special kind of atomic force microscope to control the spacing of the surfaces, they found that this strange attraction kicked in at an even longer distance of up to two microns and that it was accompanied by the formation of a vapor bubble in between. The surfaces’ antagonism toward liquid water creates a partial vacuum that draws them together, the group concludes in the August 3 *Nature*.

—JR Minkel

3. “The Science of Small,” Zack O’Malley Greenburg; *Forbes Magazine*; December 24, 2007.

A Love-Hate Relationship

Jeff Brinker makes microscopic structures that play off the tendency of molecules to repel or attract water. A coating inspired by the Namib Desert beetle is so hydrophobic that water bounces off it like a ball *(inset)*; a coated penny *(below)* repels water around it; a hydrophilic film coating can turn water into words.

Appendix D: Testimonial

NASDAQ: LUNA

LUNA INNOVATIONS®

3157 State Street
Blacksburg, VA 24060
Main: 1.540.552.5128
Fax: 1.540.951.0760
www.lunainnovations.com

C. Jeffrey Brinker
Fellow Sandia National Laboratories
Professor of Chemical and Nuclear Engineering and Chemistry
University of New Mexico
AML - 1001 University Blvd. SE
Albuquerque, NM 87106

Re: R&D 100 Award Nomination

Dear Dr. Brinker

This letter is to support the nomination to receive an R&D 100 Award for the invention of transparent superhydrophobic self cleaning coatings. Luna Innovations Incorporated has taken this technology discovered by Sandia National Laboratories / University of New Mexico and have enhanced the properties to meet the requirements of specific applications. We have found this enhanced product to be unique to current product offerings on the market today with possible applications in commercial, industrial, and military areas.

The superhydrophobic coating of this invention is unique in that it possesses several properties beyond those of similar available products. The water repelling and water shedding properties are far superior to current hydrophobic materials such as silicones or Teflon^{TM}. In contrast to conventional hydrophobic products, they are completely transparent in the visual spectrum, making them applicable to optical applications such as windows for buildings and vehicles. They can also be applied by simple techniques to any substrate eliminating the limitations of current products. These coatings have demonstrated the ability to be patterned by lithographic or other techniques to achieve a superhydrophobic – superhydrophilic surface that may find use in micro/nano electromechanical and similar devices. Preliminary cost analysis of these materials has demonstrated competitive economic viability of the product.

Luna Innovations is currently using this technology in several research and product development efforts. Ongoing development is proceeding in our facilities with aircraft coatings (corrosion inhibition), vehicles (self cleaning surfaces, rain resistance), military (self cleaning for optical and antenna resolution applications), textiles (stain resistance, rain repellency), masonry (self cleaning), wind turbines (anti-icing), and medical devices (biofouling resistance). Luna is currently in negotiations with UNM/Sandia intellectual property department for licensing the original patent (pending) of the technology. We also have a jointly applied patent pending with UNM on a complementary technology and have applied a separate related patent.

We highly encourage the consideration of this technology for a R&D 100 award.

Regards

Bryan Koene

Bryan Koene, Ph.D.
Senior Research Scientist
Luna Innovations

Sandia is a multiprogram laboratory operated by Sandia Corporation,
a Lockheed Martin Company, for the United States Department of Energy's
National Nuclear Security Administration under contract DE-AC04-94AL85000.
SAND2008-2215W. Designed by the Sandia Creative Group. (505) 284-3181. SP•124447•04/08