STUDENT BACKGROUND READING FOR EXPERIMENT D: SUPERHYDROPHOBIC MATERIALS

The aim of this experiment is analyse some innovative materials that are highly water repellent, stain less and require less cleaning thanks to their surface nano-engineering. Those materials have been developed using Nature as an inspiration, since some plant leaves have exceptional properties due to their surface composition. The property that is here analysed is the *superhydrophobic effect* found in some leaves, such as the lotus leaf. The effect is due to **interplay of surface chemistry and surface topography at the micro- and nano-level**.

In this experiment you will:

- study and **test the properties of a lotus leaf** (or another type, the nasturtium leaf, which has similar properties);

- learn about functional nanomaterials that have been engineered at the nanoscale to be superhydrophobic: a **porous silicon wafer** under study at iNANO (analysis is done by watching a video); and a fabric (from Nano-Tex, Inc.). You will **test Nano-Tex®** fabric to see how it performs compared to a normal piece of cotton fabric and compared to a lotus leaf.

In this document we will give you the background information for this experiment: we will review some fundamental concepts of surface properties, and then see how natural materials can become inspirational to some new advanced materials that totally repel water!

1. SURFACE PROPERTIES

The surface properties of a material are largely related to **chemical species that are present at the surface**. A very important surface property it its wetting behaviour, that is, how water interacts with the surface. This property is related to the terminal groups of the molecules at the surface interface, which can be either hydrophilic ("water-loving") or hydrophobic ("water-hating"). Think of what happens when you put oil in water - the oil will tend to agglomerate and form one big droplet and rest on the surface of the water. This is because water is

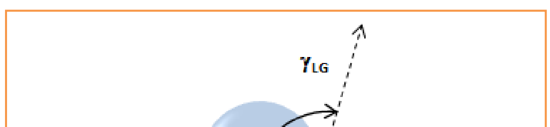

Figure 1. Static contact angle measurement of a droplet of water sitting on a flat solid surface. (Image credit: iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0)

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hydrophilic, but oil is hydrophobic. The two liquids try to minimise their contact.

One of the methods to quantify the wetting behaviour of a surface is to measure its contact angle (CA). The contact angle is the angle at which a liquid/vapour interface meets the solid surface as illustrated in **Figure 1**. The contact angle provides **information on the interaction energy between the surface and the liquid**.

The contact angle θ can be measured using an instrument called contact angle **goniometer**. This is a static measurement of contact angles. A droplet of water is deposited over the surface under investigation and the angle θ measured either manually or, in modern instruments, digitally, by capturing a digital image and using dedicated software.

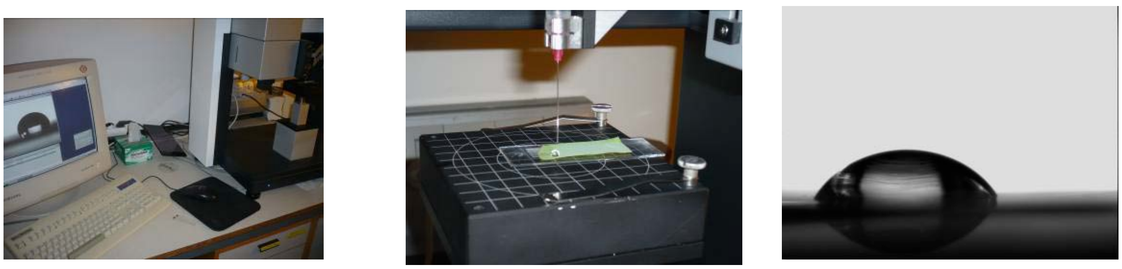

Figure 2. A contact angle goniometer with digital measurement capabilities. (Images credit: iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0)

Surfaces can be classified depending on their contact angle as illustrated in the table below.

Contact angle value	Type of surface	Example
~0	Super-hydrophilic	UV irradiated TiO_2
< 30	Hydrophilic	Glass
30-90	Intermediate*	Aluminium
90-140	Hydrophobic	Plastic
140>	Superhydrophobic	Lotus leaf

* If the value is towards 30 it is defined as hydrophilic, if it is towards 90 is defined hydrophobic

Hydrophilic means "water-loving", and hydrophobic means "water-hating". The larger the contact angle, the more hydrophobic a surface is. Think of what happens if you put water on a piece of glass: the water droplet will spread out all over the glass and the contact angle will be close to 0°. The water droplet will be so flat that the measurement of the CA is actually difficult.

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On most hydrophilic surfaces, water droplets will exhibit contact angles between 0° and 30°.If the droplet is placed on less strongly hydrophilic solids, such as a piece of metal, it will have a contact angle up to 90° or larger depending on the material. Highly hydrophobic surfaces have water contact angles as high as 150° or even nearly 180°. **These surfaces are called superhydrophobic. On these surfaces, water droplets simply rest on the surface, without actually wetting it to any significant extent.**

Surfaces with nanostructures tend to have very high contact angles, which can reach the super-hydrophobic level. This can be understood by imagining that a surface with nano-roughness is formed of a series of very small pillars. When a droplet rests on this "mat of pillars" it is in contact with a **large fraction of air**. If we think of the ideal case of a single droplet of water in air, it will have a totally spherical shape (θ = 180). For a droplet of water on a surface with a large air fraction, the larger this fraction, the closer we get to this "ideal" situation.

2. LEARNING FROM NATURE: THE LOTUS EFFECT®

Material scientists have long used different chemicals to change the properties of a various surfaces. Think of metal kitchen utensil such as cooking pan: a layer of Teflon, which is a type of plastic, is added to the metal surface of the pan to make it non-stick.

Surface chemistry can however only be used to make hydrophobic surfaces. **To reach the superhydrophobic condition, it is necessary to insert topography into the surface, such as a micro- or nanopattern**

Superhydrophobicity is a surface property found in nature, for instance in some leaves, as in the lotus leaf, and in some animals, as in the legs of water striders.

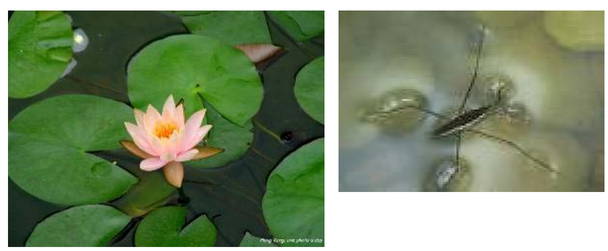

Figure 3. Two examples of natural materials that exhibit the lotus-effect: (left) a water strider (Image: Izabela Raszkova, Wiki commons, Creative Commons Attribution ShareAlike 3.0); (right): a Lotus leaf (Image credit: iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0).

How does it work? The lotus plant (*Nelumbo Nucifera*) is a native Asian plant which has the distinctive property of having its leaves particularly clean even if its natural habitat is muddy. For this reason it is regarded as a symbol of purity. The leaves of the lotus plant have the outstanding characteristic of **totally repelling water because they are superhydrophobic.** The consequence is that water droplets roll off the leaf surface and in doing so they

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drag dirt away from it. This effect, called “self-cleaning”, renders the lotus leaf clean and resistant to dirt. The **same effect is found in other leaves** such as those of nasturtium and some Canas.

Figure 4. (Left) A nasturtium plant (Image credit: Wiki commons, Creative Commons Attribution ShareAlike 3.0) and (right) a water droplet resting on the surface of a nasturtium leaf. (Image credit: A. Otten and S. Herminghaus, Göttingen, Germany, NISE Network, reprinted under NISE network terms and conditions).

How is this “nano”?

Detailed SEM analysis of leaves that display the lotus-effect has revealed the presence of wax nanocrystals on the leaf surface. **These crystals provide a water-repellent layer, which is enhanced by the roughness of the surface, making it a superhydrophobic surface, with a contact angle of about 150**. The result is that water droplets interfacing with such a leaf are in contact with a large fraction of air. This forces the water to bead and roll off. The image below shows the progressive magnification of a nasturtium leaf. In the last image on the right **nanocrystals few tens of nanometres** in size are shown.

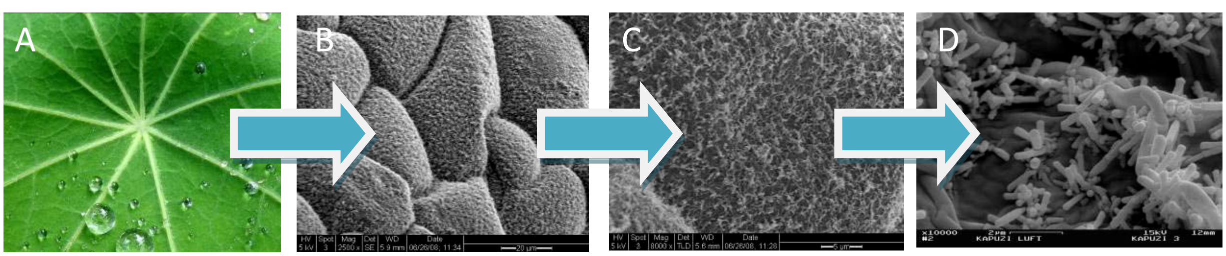

Figure 5. Close-up views at progressive magnification of a nasturtium leaf revealing the presence of surface nanocrystals (image on the far right). (Image credit (A): A. Snyder, Exploratorium; (B, C): A. Marshall, Stanford University, (D): A. Otten and S. Herminghaus, Göttingen, Germany. All images are material of the NISE Network, reprinted under NISE network terms and conditions.)

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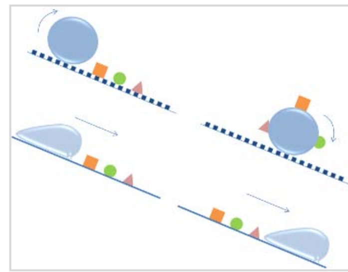
Contaminants on the surface (generally larger than the cellular structure of the leaves) rest on the tips of the rough surface. When a water droplet rolls over the contaminant, the droplet removes the particle from the surface of the leaf (**Figure 6**).



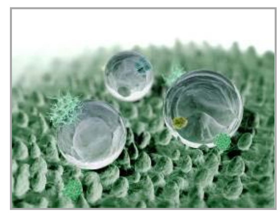


Figure 6. (Top) Diagram summarising the connection between roughening and self-cleaning: in the top image a droplet of water removes dirt from a surface thanks to the Lotus Effect (bottom): Graphical representation of contaminants and water droplets on a lotus leaf (Image credit: by William Thielike, Wiki Commons, Creative Commons ShareAlike 3.0.)

NEW ADVANCED MATERIALS AND THEIR APPLICATIONS

The Lotus Effect® has been an **inspiration for several innovative materials**, such as paints, coatings, and textiles. The realisation that certain surface properties can induce water repellence is important in numerous applications. Material scientists are now engineering numerous types of materials to render them superhydrophobic. The **main areas of applications are**:

- **Environmentally friendly coatings** and textiles that are dirt repellent and **require less cleaning**. This includes materials such as façade paints, textiles (including personal clothing) and sanitary coatings. In all these materials the added advantage is that less cleaning is needed (therefore less detergents and waste water), with a consequent benefit for the environment.

- **Improving the performance of solar cells (energy application)**. One of the problems with this technology is that they are kept outdoors and therefore can become very dirty. This layer of dirt "masks" the catalytic areas of the solar cells and therefore reduces their efficiency and lifetime. Coating the solar panel with a superhydrophobic coating keeps it considerably cleaner. Because of the nano-surface roughness, the coating is transparent to UV light, a necessity for these types of devices. The superhydrophobic coating is also durable, which further improves the solar panel lifetime.

These are not the only areas of applications. Another important one is in the **nanomedicine** sector where nano-engineered superhydrophobic surfaces are used to improve **microarray technology**.

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PRODUCTS EXAMINED IN THIS LABORATORY EXERCISE:

1. NANO-TEX®.

There are many instances where avoiding the wetting of a surface is an advantage, for instance in **textiles**, which are routinely stained by liquids (juices, coffee etc) and solids (mustard, ketchup etc). Some companies such as Nano-Tex, Inc. are now commercialising textiles that are engineered to confer superhydrophobic properties on their textiles **(Figure 7)**. This effect is obtained by the presence of "nano-sized whiskers" on the surface of the fibres that compose the fabric.

In this experimental module you will analyse and test a superhydrophobic textile from Nano-Tex, Inc. and compare it with a real lotus leaf. You will stain a piece of fabric using liquids and solids (such as ketchup, mustard etc.)

Figure 7. Liquid staining on a Nano-Tex® fabric. (Image credit: image courtesy of Nano-Tex, Inc., Copyright Nano-Tex. Inc)

How does it work? Nano-Tex® Resist Spill fabric is engineered to mimic the Lotus Effect®. This is achieved though a large number of very small "pins" or "whiskers" on the surface of the fibres. Therefore the fabric does not contain a surface coating (which could be removed by washing or sweating), but rather the fibres are nano-engineered. The result is a material which is super-hydrophobic, as illustrated by the contact angle measured and shown in the **Figure 8**. A picture of the contact angle of a lotus leaf is shown for comparison.

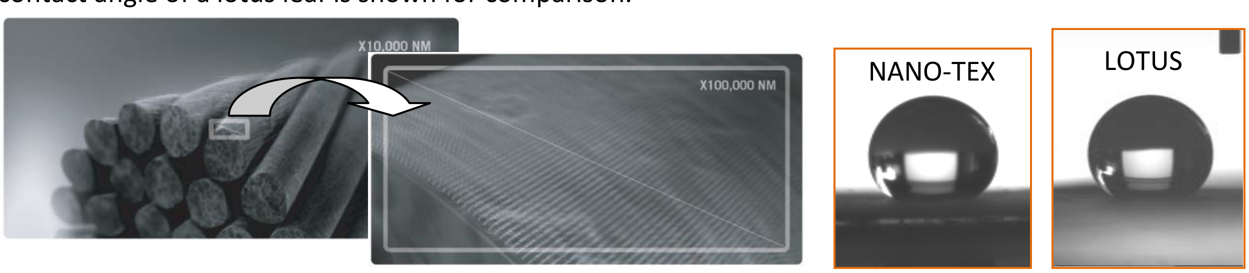

Figure 8. Left: High resolution images of the Nano-Tex® fabric (Images courtesy of Nano-Tex, Inc., Copyright Nano-Tex. Inc). Right: contact angle images of water droplets on Nano-Tex fabric and Lotus leaf (Images: iNANO; Aarhus University, Creative Commons Attribution ShareAlike 3.0).

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2. POROUS SILICON

The second material that is analysed in this experiment is a material under research at iNANO in collaboration with Lund University which is made of **porous silicon. You will see the behaviour of this material through a video.**

As mentioned above, surfaces (or textiles) engineered to be superhydrophobic are made of very small "pins" or "whiskers" inspired by the microstructure of the lotus leaf. The **porosity and spacing of this fine structure determines the wetting properties of the material**. The material shown in the video has a contact angle of 167.

The superhydrophobic effect results from the particular micro/nanotexture of this surface.

In this experiment you will see how porous silicon compares with a real lotus leaf in terms of wetting through a video.

Figure 9. Images from NANOYOU Video 4-"Lotus Effect-Part 2" showing the wetting properties of a piece of porous silicon (left) and how this material compares with a real lotus leaf (right). (Image credit: iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0)

How does it work?

Surfaces engineered to be superhydrophobic are made of very small "pins" inspired from the microstructure of the Lotus leaf. The porosity and spacing of this fine structure determines the wetting properties of the material. To do so, scientist modify the surface of normal silicon (which is normally hydrophilic) with specialized methods.

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Figure d10 shows some samples of **porous silicon**, which can be engineered to be superhydrophobic. In Figure d10, sample A is normal silicon (untreated) and samples B, C and D are porous silicon samples obtained with different fabrication conditions. **Table 2** summarizes the contact angle of each sample.

Sample	Contact Angle (°)
A	64
B	110
C	155
D	167

Table 2

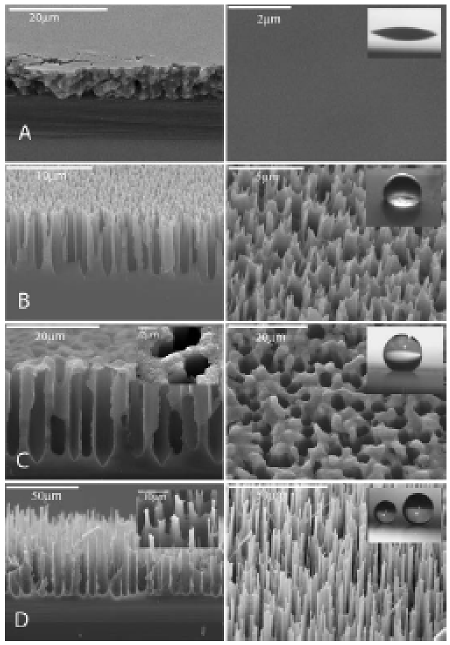

Figure d10. SEM Images of four different samples showing a change in contact angle from hydrophilic (A) to hydrophobic and superhydrophobic. Samples B-D are made of porous silicon, sample D is the one with the higher contact angle (Image reprinted with permission from: A. Ressine, "Development of protein microarray chip technology", PhD thesis 2005)

The sample of porous silicon shown **in the video is sample D**. As seen from Figure d10 and Table 2 this is the most superhydrophobic with a contact angle of 167. What is interesting to note is that in sample B the distance between the "pillars" is smaller than in sample D, so the porosity (percentage of voids in the material) is lower. Therefore in sample D there is a larger "fraction of air" to which the droplet is exposed, and the contact angle is larger. This examples shows that to engineer superhydrophobic surfaces scientists need to find the right fabrication conditions to obtain the right balance of "nano-pillars" and porosity within the silicon surface. It is this balance of micro and nanotexturing that leads to superhydrophobic materials.

The surface of the superhydrophobic porous silicon remarkably resembles that of a water strider, which also displays a micro-/nanotextured surface. Notably, the contact angle of the water strider leg is also 167 C.

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CREDITS: Experiment is partly adapted from the Application activity: Nano-Tex, http://mrsec.wisc.edu/Edetc/IPSE/educators/nanoTex.html.We thank Nano-Tex, Inc. for their courtesy in providing a piece of their Nano-Tex® textile (Resists Spills), and for providing images of this material. Thanks to Anton Ressine (iNANO, Aarhus University) for providing the porous silicon sample shown in the videos of this experiment.

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