STUDENT LABORATORY WORKSHEET

EXPERIMENT D: SUPERHYDROPHOBIC MATERIALS

Student name:……………………

Date:…………………………………..

AIMS:

- Understanding the concept of hydrophobic and hydrophilic materials.
- Examining natural superhydrophobic surfaces versus common surfaces.
- Testing novel advanced materials that have been engineered to be superhydrophobic, by mimicking natural materials at the nanoscale, and comparison with everyday materials.

MATERIALS:

- Different surfaces to test:
  * 1 microscope glass slide
  * 1 flat piece of plastic 10x10 cm (e.g., cut a piece out of a smooth plastic sheet such as a plastic folder, or use a CD.)
  * 1 flat piece of aluminium foil 10x10 cm
  * 1 piece of filter paper
  * Pieces of textiles to compare (about 10x10 cm):
    - 3 pieces of Nano-Tex® Resist Spills fabric
    - 3 samples of 100% cotton
    - 2 samples of fabric made with synthetic fibre such as polyester or cotton/poly blend; in this protocol we used a fabric with 70% polyester, and 30% cotton)

- Different stain agents to choose from
  * 1 glass of water,
  * 1 glass of juice and/or 1 glass of coke
  * Balsamic vinegar or wine (1 glass)
  * cooking oil (1 glass)
  * Ketchup (1 spoon)

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

* Mustard (1 spoon)
* Mayonnaise (1 spoon)
* Organic soil (a couple of handfuls)

- Different plant leaves (collect from school garden or bring from home)
  * One common plant leaf such as ivy
  * One piece of Lotus leaf or Nasturtium
- Laboratory bottle filled with water
- Eyedroppers (or Pasteur pipettes) to apply the liquid stain agents - Plastic knives or spoons to apply the other stain agents
- A bucket with laundry detergent and water (you might need to share this with the entire class)
- 1 permanent marker
- Several plastic cups to hold water and stain agents
- Several plastic plates to put materials in when conducting the material testing
- Paper glue and scissors

SAFETY NOTE: This experiment doesn't use chemicals but only common liquids and solids. Nevertheless staining is possible so wash hands and surfaces thoroughly after handling. Use appropriate clothing protection, gloves and eyes protection. Collect all liquids and washing water in glass/plastic containers and dispose in water basin. All experiments will be carried out at your own risk. Aarhus University (iNANO) and the entire NANOYOU consortium assume no liability for damage or consequential losses sustained as a result of the carrying out of the experiments described.

PROCEDURE

You will now test a series of materials, starting from common ones and moving towards more advanced ones. When you test the materials with water or other liquids, do so by placing the material inside a plastic plate in order to collect the water neatly. **Dispose of the collected water in between stages of the tests**.

PART 1: Understanding surface properties: from hydrophilic to superhydrophobic

An important surface property of a solid material is its wetting behaviour, that is, how liquids interact with the surface. On any two surfaces water droplets may:

- Have different shapes,
- Be absorbed or be repelled,
- Tend to move or slide differently over a surface with a slope.

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

Part 1a: The shape of the droplet

Place in plastic plates the six surfaces that are to be tested: **a glass slide, a piece of plastic, a square of aluminium foil, a square of filter paper, and one leaf of each type. Place a couple of droplets of water on each material.**

Q1. What are the shapes of the droplets on the different surfaces? Fill the table below by drawing the **shape** of the droplets:

Material	Shape (profile) of the droplet
Aluminium	
Plastic	
Filter paper	
Glass	
Common leaf	
Nasturtium/lotus leaf	

Q2. Describe in your own words the differences in the droplet's shapes.

………
………
………

In your opinion, what could explain these differences?
(Refer to answers given in the warm up activity)

………
………

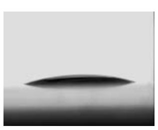
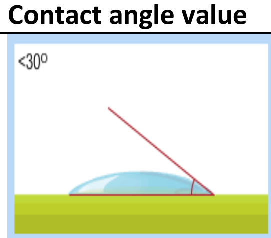
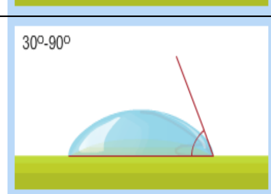
The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

Part 1b: From water "lovers" to water "haters"

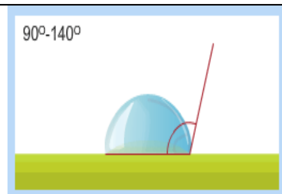
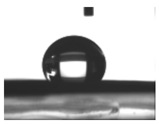
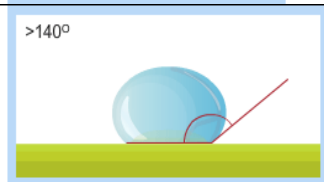
The behaviour of water on the surface is related to the part of the molecules displayed at the surface interface, which can be either hydrophilic ("water-lover") or hydrophobic ("water-hater"). Think of what happens when you put oil in water - the oil will tend to agglomerate and form one big droplet and rest on the surface of the water. This is because oil is hydrophobic, and the two liquids try to minimize their contact.

There are several aspects to the behaviour of water on the surface of a material, but one of these behaviours can be used to **quantify** the wetting behaviour: While observing the shape of the droplet on the surface, it is possible to measure the contact angle, the angle at which a liquid droplet meets the solid surface as illustrated in the table below. The more the surface "hates" the water, the more the droplet of water will roll up in a bead to try to minimize the contact with the surface. **Surfaces can be classified depending on their contact angle as illustrated in the Table below, ranging from hydrophilic to intermediate, hydrophobic to superhydrophobic surface**

Q3. According to the experiment from Part 1.a and the explanation above, fill in the missing data in the following table:

Shape (profile)	Contact angle value	Type of surface	Materials
			
			

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

Q4. The filter paper behaved unlike the other materials - in what way?

………

………

Q5. How do you think we can decide whether the filter paper is hydrophobic or hydrophilic?

………

………

As we can see, the fact that a material is a "water lover" or a "water hater" can be observed by looking at the shape as well as the absorbency (as seen in the case of the filter paper)

Part 1c: The sliding of the droplet

Choose the two most hydrophobic surfaces (hint: the Nasturtium/lotus leaf should be one of them). Use a spoon or a Pasteur pipette to pour some water over each surface, raise one side of the surface a bit and observe how water slides or rolls off the surface.

(A container should be used to collect the water, and a paper towel should be on hand).

Q6. Do the water droplets wet the surfaces (i.e., is water left over the surfaces once you stop pouring it)? What indication do you have?
Give an answer for each type of surface you have tested.

………

………

Q7. Do the water droplets roll or do they slide over the surfaces?

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

………
………

Pour some more water on each of the two surfaces and hold them horizontally in your hands

Q8. Can you get a droplet to rest still over the surface on each of the materials? Is it easy or difficult? Describe what you see.

………
………

Hydrophobic vs. superhydrophobic: On a hydrophobic surface the water droplets are repelled from the surface ahead of them. This affects the way that water moves on the surface. On a superhydrophobic surface, however, the water is repelled so strongly that it seems that there is no longer any interaction between the droplets and the surface, and the drop just rolls around freely, almost like a bead on the surface.

Q9. Based on all the above observations and information, which is the most hydrophobic surface of the two? Explain.
Is this consistent with the drop shapes that were used to assess these types of surfaces?

………
………

Q10. Write your conclusions for this experiment: (relate to each part of the experiment)

………
………

PART 2- Analysis of a functional nanomaterial.

As you have seen in the first experiment, the leaves of the Lotus plant have the outstanding characteristic of **totally repelling water, they are superhydrophobic.** The consequence is that water droplets roll off the leaf surface and in doing so they drag dirt away from it. This effect, called "self-

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

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.

How does this work? This is nano! Detailed scanning electron microscopy (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: Water droplets on such a leaf are in contact mainly with the air that is trapped between "nano-pillars" underneath the droplet. If we think of the ideal case of a single droplet of water hanging in air, it will have a totally spherical shape. For a droplet of water on a surface with nanostructures, **the more air trapped in the surface under the droplet, the closer we get to this "ideal" spherical situation, making it a superhydrophobic surface.**

In the case of the lotus leaf the droplet has a contact angle of about 150°, which 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 a few tens of nanometres** in size are shown.

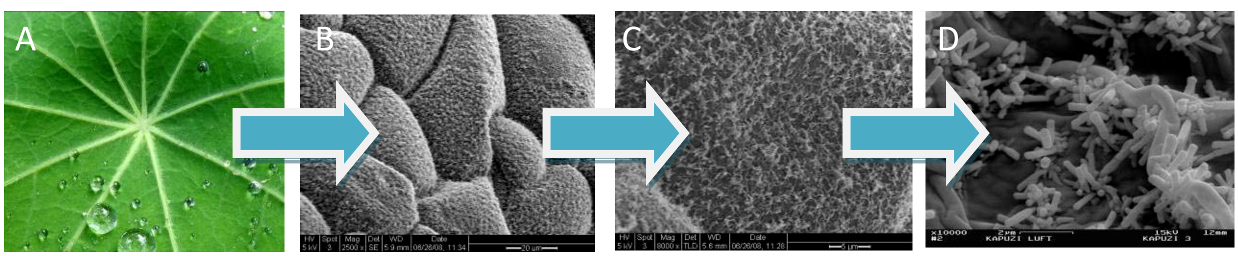


Figure 1. Close-up views at progressive magnification of a nasturtium leaf revealing the presence of surface nanocrystals (image on the far right). (Image credit (A): A. Snyder, Exploratorium; (B, C): A. Marshall, Stanford University, (D): A. Otten and S. Herminghaus, Göttingen, Germany, all images are material of the NISE Network, www.nisenet.org, reprinted under NISE network terms and conditions.)

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

Learning from Nature: The Lotus Effect®. Material scientists have long used different chemicals to change the surface properties of certain surfaces. Think of metal kitchen utensils such as cooking pans: 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, however, can only be used to make hydrophobic surfaces, and not superhydrophobic ones. And yet, superhydrophobicity is found in nature, for instance (as seen in this experiment) in some leaves, such as the Lotus leaf, and in some animals, as in the legs of water striders (see Figure 2).In these natural materials like the Lotus leaf the superhydrophobicity is the result of an interplay of chemistry (wax crystals on the surface of the leaf) and nano-topography (dimensions, shape, inter-distance of the nanocrystals).

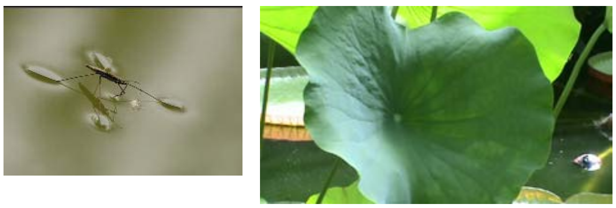


Figure 2. Two examples of natural materials that exhibit the lotus effect: (left) a water strider (Image: Izabela Raszkova, Wiki commons, Creative Commons Attribution ShareAlike 3.0); (right): a Lotus leaf (Image credit: iNANO, Aarhus University, Creative Commons Attribution ShareAlike 3.0).

The Lotus Effect® has been an inspiration for several innovative materials, such as paints, coatings and textiles. Some companies such as Nano-Tex, Inc. are now commercializing textiles that are engineered to confer superhydrophobic properties on their textiles. This effect is obtained by the presence of "nano-sized whiskers" on the surface of the fibres that compose the fabric.
In this part of the experiment you will analyse a textile that has been engineered to replicate the Lotus Effect®

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 detergent and waste water), with a consequent benefit for the environment.

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

- **Improving the performance of solar cells (energy application)**. One of the problems with this technology is that these cells are kept outdoors and therefore prone to become very dirty. This layer of dirt "masks" the catalytic areas of the solar cells and therefore reduces their efficiency and life-time. Coating the solar panel with a superhydrophobic coating keeps the panel 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 life-time.

2a: Interaction with water

Place one piece of Nano-Tex® and one piece of a normal cotton fabric in a plastic plate and pour some water over them.

Q11. Which material from Part 1a does the Nano-Tex® fabric behave like? In what way? Which material does the cotton behave like?

………

………

2b: Interaction with different liquids

Now in order to test the applications of the Nano-Tex® fabric we compare it with normal cotton and with a semi-synthetic fibre. For this you need **in total** two pieces of cotton fabric, two pieces of a semi-synthetic fabric, and two pieces of Nano-Tex® (each about 10x10 cm). **Follow the steps below**.

STEP 1 - The "stain effect"

Testing the effect of liquids (coke, vinegar, oil, etc.) and thick liquids (mayonnaise, mustard, etc.).

In order to do this experiment prepare a glass of each liquid you want to test, as stated below:

- Choose two types of liquids (from juice, coke, vinegar, wine, and oil).
- Choose two types of thick liquids (from ketchup, mustard, mayonnaise).

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

Place your three pieces of different fabrics in a row, left cotton, middle semi-synthetic, right Nano-Tex®. Write on a piece a paper the type of fabric and place it below each fabric (as in the image below).

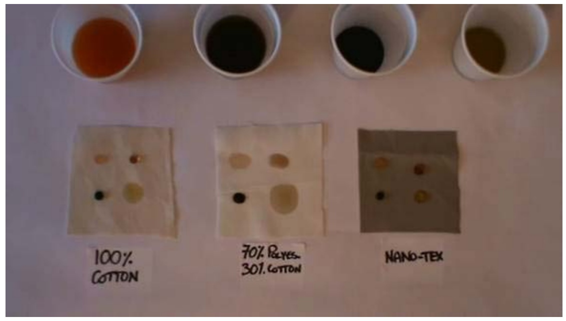
Decide in which order you will place the liquids and write it down:

Liquid 1 _________	Liquid 2 ________
Thick Liquid 1 ___________	Thick Liquid 2 ___________

With the aid of a pipette or an eye-dropper, place a droplet of each liquid to be tested on each fabric. Use a spoon or spatula to place the thick liquids on the fabric. On an available area mark it with a permanent marker.

To compare the fabrics you must define a set time of staining for this experiment (e.g., 5 min.). Indicate it on the table below.

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433



After the set time, gently remove the liquids from the fabric by blotting it with a piece of kitchen paper. Use a wet cloth to remove the thick liquids from the fabrics. Be careful not to mix the different liquids.

Note:
All materials that is tested should be saved for further testing

Q12. Record your observations in the table provided.
In each cell refer to two aspects, where there can be three levels within each aspect:
Absorbed: Not at all, a bit, a lot
Stained: Not at all, a bit, a lot

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

	Time of liquid staining: ………..seconds (*fill in*)				
Material/ chosen liquid	**1** **liquid 1** **(for example juice)**	**2** **liquid 2**	**3** **thick liquid 1** **(for example mustard)**	**4** **thick liquid 2**	**Marker**
Cotton fabric					
Semi-synthetic fabric					
Nano-Tex					

Q13. Was there a difference between the fabrics? Elaborate

………

………

Q14. Did all stains come off the **Nano-Tex®**? Elaborate

………

………

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

STEP 2- The "dirt effect"

In this step organic soil is used to compare Nano-Tex® fabric with normal cotton and with a semi-synthetic fabric.

Take three clean, dry pieces of fabric, one for each type, and place some organic soil in the middle of each fabric. Fold the fabric and rub it, and then open each piece of fabric, remove the soil from each, and observe.

Note:
All materials that are tested should be saved for further testing

Q15. Did all the fabrics get dirty in the same way? Describe.

……

……

Now try to clean the fabrics with your hands.

Q16. Could you clean the fabrics? Is there a clear difference among them? If so, describe which type of fabric could be cleaned more easily.

……

……

Q17. Was there a fabric that could be totally cleaned and appeared as new?

……

……

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

STEP 3 - "Cleaning level"

Testing for ease of cleaning.

Now try to clean the three fabrics used in STEPS 1 and 2 with cold water and soap.

Q18. Do all fabrics become clean? If not, which one does?

………

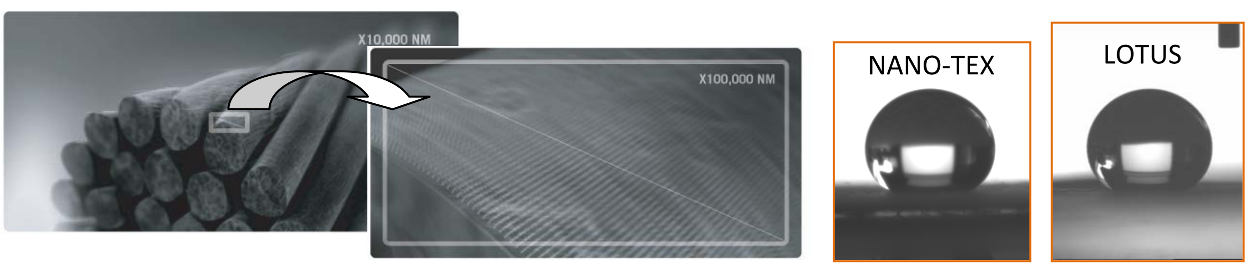
Q19. Which type of fabric could be cleaned most easily?

………

Q.20. Is there one type (or more) of stain that doesn't come off from the Nano-Tex® samples? Which one? Why do you think this is?

………

How does it work? Nano-Tex® fabric is engineered to mimic the Lotus Effect®. This is achieved through 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 3**.



* A picture of the contact angle of a lotus leaf is shown for comparison.

Figure 3. 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)**.**

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

The nanostructure of the surface that repels the water droplets (as well as other liquids) explains the self cleaning phenomenon.

When a water droplet rolls over the contaminant, the droplet removes the particle from the surface of the leaf, in contrast to a drop that slides over the surface, leaving particles behind (**Figure 4**).

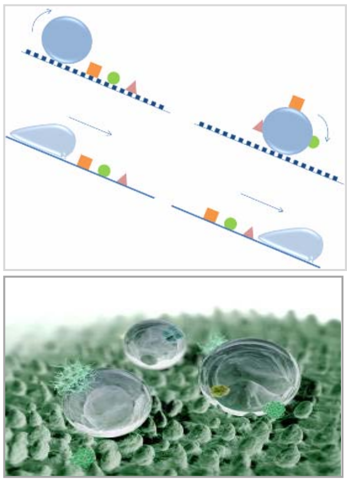


Figure 4. (Top) Diagram summarizing the connection between roughening and self-cleaning: in the top image a droplet of water removes dirt from a surface thanks to the Lotus effect (bottom): Graphical representation of contaminants and water droplets on a lotus leaf (Image credit: by William Thielike, Wiki commons, Creative Commons ShareAlike 3.0)

Q21. Write your conclusions for Part 2 of this experiment:

……

……

……

……

Q22. What are possible applications of nanomaterials? **Explain.**
(Compare and discuss with whole class)

……

……

……

Watch with your teacher the video ***NANOYOU Video 4: Lotus Effect® - Part 2***

In this video you will an engineered surface made of porous silicon that is under development in the laboratories of iNANO, Aarhus University, and that mimics the properties of the Lotus leaf.

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433

Discuss with your teacher the applications where you think such properties could be useful.

CREDIT NOTE:
This experiment is partly adapted from the Application activity: Nano-Tex, http://mrsec.wisc.edu/Edetc/IPSE/educators/nanoTex.html.

ACKNOWLEDGEMENTS:
We thank Nano-Tex, Inc. for their courtesy in providing a piece of their Nano-Tex textile (stain and spill resistant), and for providing images of this material.
The author wishes to thank Anton Ressine (iNANO, Aarhus University) for providing the porous silicon sample shown in the videos of this experiment.

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 233433