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The Mechanism of Hydrogen Bubble Formation Caused by the Super Hydrophobic Characteristic of Taro Leaves

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Abstract – *This study is aimed at uncovering the mechanism and role of the super hydrophobic characteristic of taro leaves on the process of hydrogen gas formation when there is a contact with a water droplet. The investigation was organized as: SEM-EDX analysis on the surface of taro leaf, observation on gas bubbles within a water droplet on the surface of taro leaves, and the detection of hydrogen gas production. The study result shows that the super hydrophobic characteristic of taro leaves caused the formation of great contact angle and high surface tension energy in droplets. A pointed-shaped nano texture caused the tension energy of the droplet surface to increase. As a result, particles randomly vibrate triggering the reaction between H_2O droplets and Mg, K, and Ca on the surface of leaves producing hydrogen gas bubbles. Some gas was trapped in the nano grooves on the leaves surface and some with high pressure broke through the droplet and then were driven out by the Brownian motion.*

***Keywords**: Super Hydrophobic, Taro Leaves, Water Droplets, Hydrogen Bubbles*

I. Introduction

The behavior of animals and plants is very interesting to observe, especially when they are adaptating to their environment. The anatomical form, together with the surface structure, has a uniqueness that still is the secret of nature. Animals and plants on earth provide a variety of material examples, surface forms and structures (replica) in which the features are replicable for practical application [1].

Based on some research, it shows that there are several plants having typical characteristics, such as: being able to convert chemical energy, possessing superhydropobic, hydrophilic, adhesive characteristics, and being able to show responsive movements when there is some stimulation [2]. Many experts on biology and materials started researching on plants superhydropobic characteristic. A uniqueness owned by the superhydropobic characteristic of plants is the ability to clean their own self up. The self-cleaning ability of superhydropobic leaves is influenced by the contact angle of hysteresis. The low contact angle of hysteresis plays an important role in self-cleaning or obstacle reduction process in fluid flow. The contact angle of hysteresis is the standard of dissipation energy during the flow of drops on the solid surface. At the low value of hysteresis contact angle, it is more likely for the drops to slide and roll wiping out the particle contaminant. At a less than 10^0 of contact angle of hysteresis, it is generally mentioned as surface able to perform the self-cleaning. The coarseness of the superhydropobic material surface and the self-cleaning ability on its surface bring up some inspiration in various applications.

A variety of superhydropobic surfaces has been produced in laboratory and even commercialized [3] – [5]. Some examples of self-cleaning products are paints, roof tiles, fabrics, and window glasses. The superhydropobic and hydropilic surface has been developed for the photoresponsive surface with inorganic oxyde and photoreactive organic molecules [6], copolymer film sensitive towards pH [7] or to electric field [8].

A leaf surface has the superhydropobic characteristic when it has a static contact angle above 150^0. The examples of leaves surface being superhydropobic are lotus and talas leaves. Both of them have the highest contact angle with water [9] – [14]. The contact angle formed on taro leaves when it touches the water droplet is 165° [15]. The water droplet can roll on the surface of taro leaves with a very little drag coefficient because of the chemical composition and the surface topography of superhydropobic leaves [16].

The microstructure of taro leaves consists of a polygonal epidermic cell with a micro-bump scale in the size of 15-30 μm and a papilla in the central part of every cell. The whole surface is covered by epicuticular crystal wax cells with nano-size consists of aliphatic compound [17], [18]. The wax crystal is shaped like some little white hair [19]. The wax layer plays an important role in the self-cleaning mechanism of taro leaves [20]. The existence of the wax layer reduces the adhesive force and drag coefficient [19].

The result of XPS analysis (X-Ray Photoelectron Spectroscopy) of the wax layer on taro leaves shows that the atomic carbon concentration is 98,21% and atomic oxygen is 1.79% [21].

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The hydropobic characteristic of lotus leaves when it is in contact with water has been studied by [22]. The study result shows that there is some gas trapped in the surface of lotus leaves having an imporant role in the superhydropobic characteristic of lotus leaves [22].

This study concludes that gas trapped is air that is trapped due to the leaf surface roughness. The hydropobic characteristic of taro leaves has been previously observed by many researchers. But, the study on the mechanism of hydrogen gas formation in water droplets when in contact with taro leaves is still rarely considered.

II. Materials and Methods

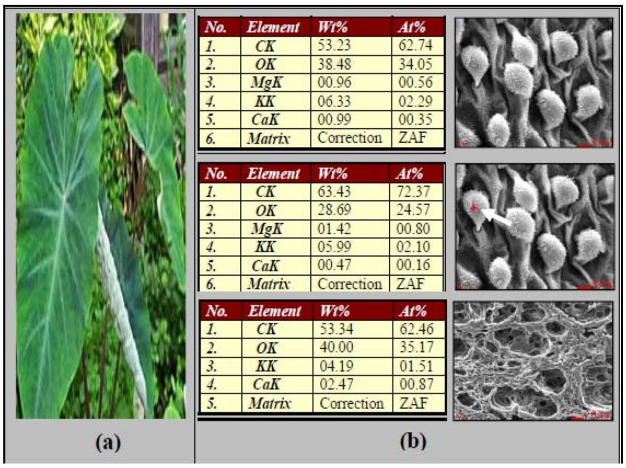
II.1. Material

The material studied was fresh taro leaves as shown in Figure 1(a). The taro plant belongs to the kingdom: *plantae*, division: *magnoliophyta*, class: *liliopsida*, ordo: *arales*, family: *araceae*, genus: *xanthosoma*, and species: *xanthosoma roseum*. The taro leaves were cleansed from dust or faces clung on their surface.

The composition and topography of taro leaves surface were examined using SEM-EDX with 1000, 5000, 10000, and 20000x magnification. The SEM instrument (Scanning electron microscope) used was Inspect S 50 FEI. Meanwhile, the experimental instrument of EDX (Energy Dispersive X-ray) used was Amatex-edax.

Figure 1(b) is the surface topography and EDX experimental research of taro leaves of the entire surface: papilla part (the arrow sign) and mesophyll layer.

The measurement results show that the surface of taro leaves contains: Carbon (C), Oxygen (O), Magnesium (Mg), Potassium (K), and Calcium (Ca). Metal elements, like Mg, K, and Ca, are highly reactive and strong oxidizing substances.



No.	Element	Wt%	At%
1.	CK	53.23	62.74
2.	OK	38.48	34.05
3.	MgK	00.96	00.56
4.	KK	06.33	02.29
5.	CaK	00.99	00.35
6.	Matrix	Correction	ZAF

No.	Element	Wt%	At%
1.	CK	63.43	72.37
2.	OK	28.69	24.57
3.	MgK	01.42	00.80
4.	KK	05.99	02.10
5.	CaK	00.47	00.16
6.	Matrix	Correction	ZAF

No.	Element	Wt%	At%
1.	CK	53.34	62.46
2.	OK	40.00	35.17
3.	KK	04.19	01.51
4.	CaK	02.47	00.87
5.	Matrix	Correction	ZAF

Figs. 1. (a) Taro leaves (xanthosoma roseum) and (b) The topography and EDX experimental result of taro leaves surface

II.2. Research Procedure

II.2.1. The Measurement of Droplet Volume and Contact Angle

The procedure for making droplets and measuring the contact angle is shown in Fig. 2. The droplets (5) were made using the syringe pump (1) with a particular volume and expelled drop by drop on the surface of taro leaves (6). Then, the contact angle of the droplet was measured using a digital microscope with the specification of: Image Sensor: 2.0 MP, focus range: 0-100mm, magnification ratio: 1000× from the position (4) using the measurement software provided in the digital microscope.

II.2.2. The Observation of Hydrogen Bubbles

The hydrogen gas bubbles were observed using the digital microscope from two positions, (2) and (3), as shown in Fig. 2. The position of the microscope (2) is vertical towards the droplet to observe the gas bubbles in the base of the droplet and position (3) is to observe the bubbles formed due to the reaction of water droplets and taro leaves.

This position is used because the appearance of gas bubbles is clearer.

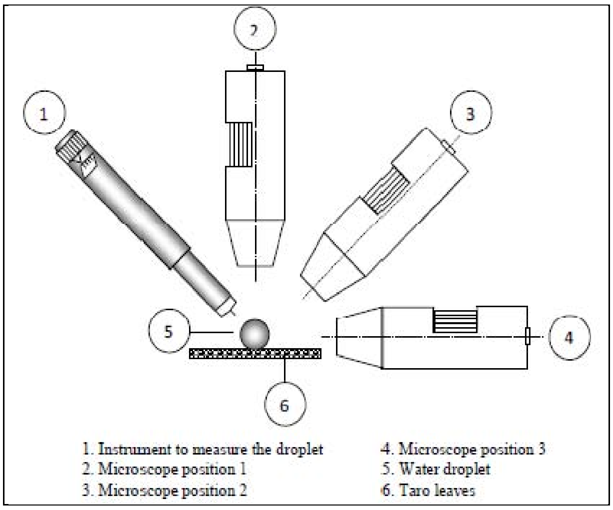


Fig. 2. Droplet measurement technique and photography done using digital microscope

II.2.3. Hydrogen Sensor and Calibration Technique

Figure 3 shows the calibration technique for a MQ-8 hydrogen sensor with pure hydrogen injected into the container (1) through silicon nipples (2) using a syringe pump (3) for every 0.25 ml up to 2.5 ml.

The measurement result of the hydrogen sensor was compared to the hydrogen concentration actually injected into the container. Every measurement was repeated a hundred times (100×) and then the result was averaged. The calibration result is shown in Fig. 4.

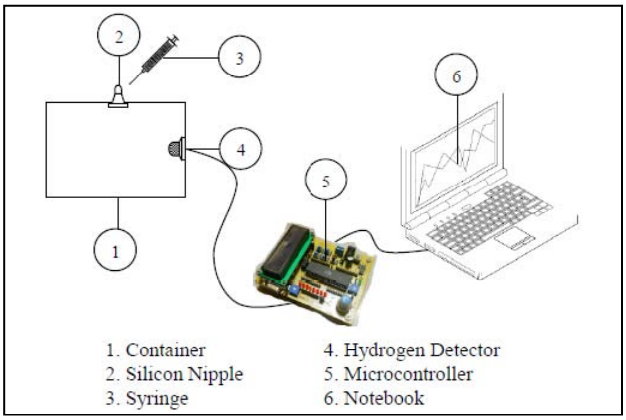


Fig. 3. The calibration setting of the hydrogen detector

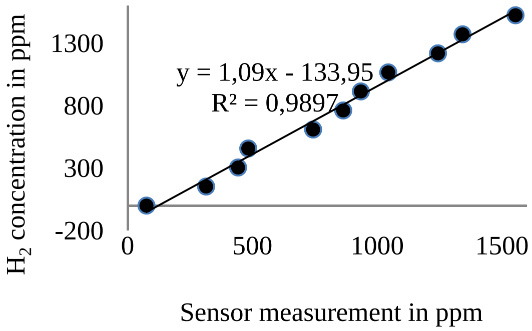


Fig. 4. The calibration result using pure hydrogen

II.2.4. Data Acquisition Using Hydrogen Detector

The hydrogen gas originating from the contact between water and taro leaves was detected using the hydrogen sensor by data acquisition system as in Fig. 5. Taro leaves (1) with areas varied as 0.04 m^2, 0.08 m^2 and 0.12 m^2 were each put into a closed container (2) filled with water (3) and the hydrogen gas production was released into the air section on its top. The hydrogen sensor (5) was put into the tube as shown in Fig. 5. The process of collecting data of hydrogen gas was done in the interval of 8 to 24 hours.

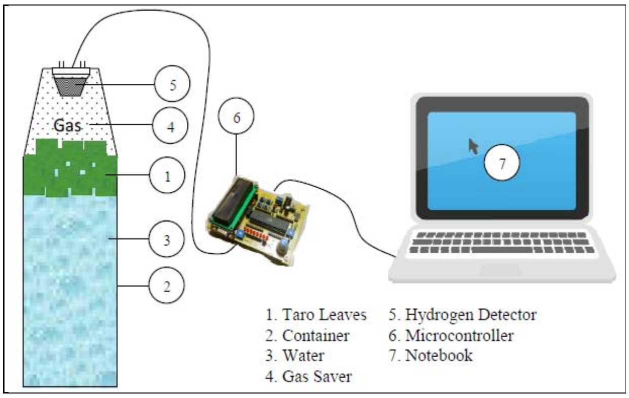


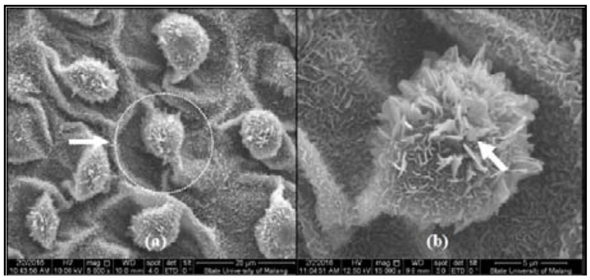
Fig. 5. Data acquisition system of hydrogen gas

II.2.5. The Hydrogen Production Verification With Gas Chromatography

The production of hydrogen gas from tube container in Fig. 5 was also verified using the gas chromatography (GC). The gas sample from container (2) was collected in the tube collector for the GC. The GC instrument *used in this experiment is GC-8A Simadzu single detector TCD.*

III. Result and Discussion

The form of taro leaves surface at the magnification of 15000x is very coarse. The coarseness of the papilla part on the surface (arrow sign) is more prominent compared to the part of epidermis cell which is polygonal (as shown in Fig. 6(a). The surface texture is indeed sharp-pointed as shown in Fig. 6(b). Papilla has the most sharp-pointed texture. The sharp-pointed texture consists of epicuticular wax crystal nano cells that results in a superhydrophobic characteristic. Based on the EDX experimental result, epicuticular wax crystal cell layers contain elements such as C, O, Mg, K and Ca as in Fig. 1(b).



Figs. 6. The magnification of taro leaves surface
(a). Polygonal epidermis cell and
(b).Papilla in the centre of every cell

The sharp-pointed nanotexture causes a very high surface tension when in contact with water droplets. The contact angles formed between the droplets and the leaves surface are 165^0, 158^0 and 148^0 for the droplet diameter of 1, 2, and 3 mm, respectively as shown in Fig. 7. The contact angle reduced as the droplet volume increased as shown in Fig. 8. The angle of 165^0 shows that taro leaves have the superhydrophobic characteristic. The large contact area makes the droplet on the taro leaves have very high surface tension energy. When the water droplet is in contact with the taro leaves surface, the texture of taro leaves which is sharp-pointed in nano-scale, then, propped up the surface of the droplet. The contact angle formed between nano texture droplets and taro leaves became larger.

Fig. 7. The super hydrophobic characteristic in taro leaves with droplet

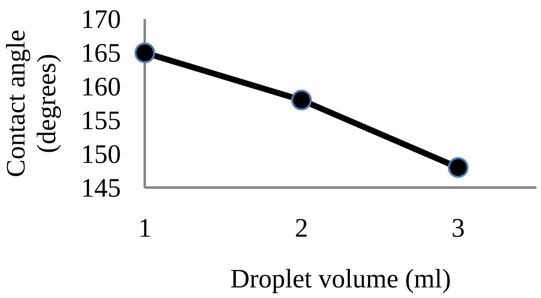


Fig. 8. The relation between droplet volume and contact angle on taro leaves

As a result, the surface tension energy on each of the sharp points with nanotexture popping up the droplet became significantly higher.

The very high surface tension energy causes reaction between H_2O droplet and the elements of taro leaves surface. The reaction follows these equations:

$$Mg_{(s)} + 2H_2O \rightarrow Mg(OH)_2 + H_2 \quad (1)$$

$$Ca_{(s)} + 2H_2O \rightarrow Ca(OH)_2 + H_2 \quad (2)$$

$$2K_{(s)} + 2H_2O \rightarrow 2KOH + H_2 \quad (3)$$

The reaction is confirmed by the formation of bubbles on the taro leaves surface as shown in Fig. 9. Gas bubbles spread across all part of taro leaves surface in contact with the droplet. According to the measurement result, the average diameter of the bubbles is 21,2μm. The bubbles diameter has the same size of polygonal epidermis cells with a micro-bump scale as shown in figure 6a (circle sign). It means that some of the hydrogen gas is trapped in the polygonal epidermis cell spaces as a result of reaction. Fig. 10 shows the movement of hydrogen gas bubbles (pointed by white arrows) in the water droplet photographed above. This movement of gas bubbles indicates two things.

First, it indicates that there was a reaction between water and the taro leaves surface on the contact point with papilla. The contact point on nano sharp points of the leaves surface stores a very high surface tension energy that triggered the reaction to produce hydrogen gas. Gas was trapped in the sharp particle spaces of papilla (Fig. 9). Gas production continually undergoing caused an increase of the volume of gas trapped so that the pressure increased as well. After pressure exceeded the surface tension of the droplet, the gas bubbles breakthrough the droplet and moved in the droplet. Second, the circling bubble movement signifies that there was Brownian motion indicating that the water molecule vibrates more intensively due to the high surface tension of the droplet. The stronger vibration of water molecule is a source of energy that promotes a reaction between the elements of taro leaves surface (Ca, Mg, and K) and water producing H_2 gas.

Figure 11 shows the gas bubbles movement photographed from the front side. It is seen that the gas bubbles move from the bottom to the top near the droplet edge. This gas bubble is from gas trapped on the leaves surface whose pressure has exceeded the surface tension of the droplet.

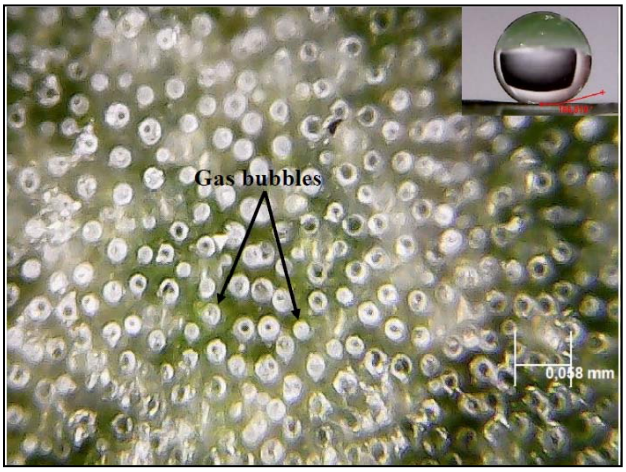


Fig. 9. Gas bubbles on the taro leaves surface when in contact with the droplet in the magnification of 1000x

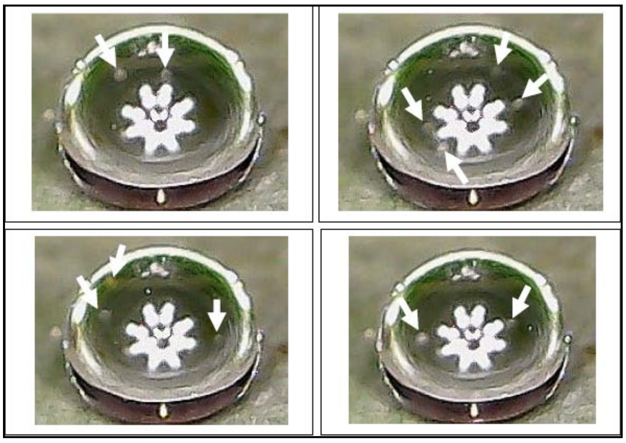


Fig. 10. The emergence of hydrogen gas bubbles

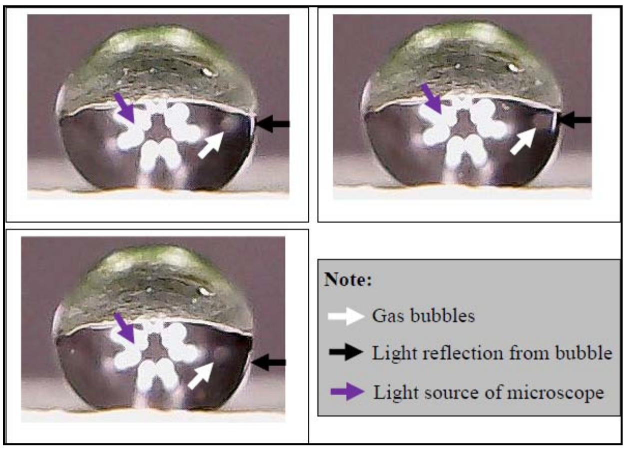
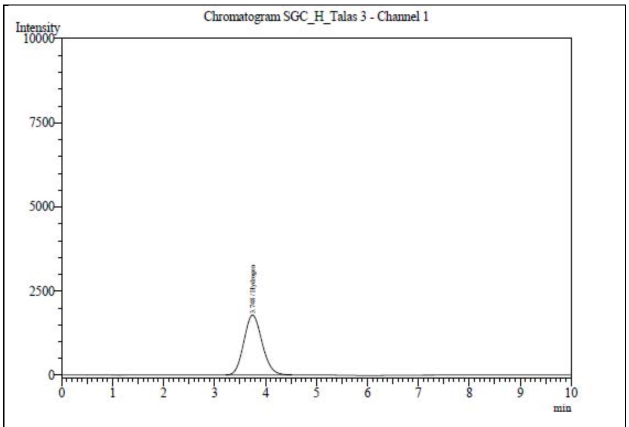


Fig. 11. Hydrogen gas formation in the droplet of taro leaves

Fig. 12 shows that the gas sample from the reaction between water droplets and the leaves surface examined with GC apparently contains hydrogen gas that is of 2,287% (22870 ppm). It assures that the water droplet has reacted with the chemical element contained in the taro leaves surface as a result of a very high surface tension called superhydrophobic. The measurement result of hydrogen gas using MQ8 sensor is depicted in Fig. 13 with the areas of taro leaves of $0.04m^2$, $0.08m^2$ and $0.12m^2$. It appears that the production rate of hydrogen gas fluctuates almost periodically. It is as a result of hydrogen gas formed and trapped in the nano particle spaces on the surface of taro leaves periodically penetrating the water droplet in the form of gas bubbles.



Peak Table - Channel 1

Peak#	Ret.Time	Area	Height	Conc.	Units	Mark	Name
1	3.748	44251	1779	2.287	%		Hydrogen
Total		44251	1779				

Fig. 12. The experimental result of gas chromatography of taro leaves gas

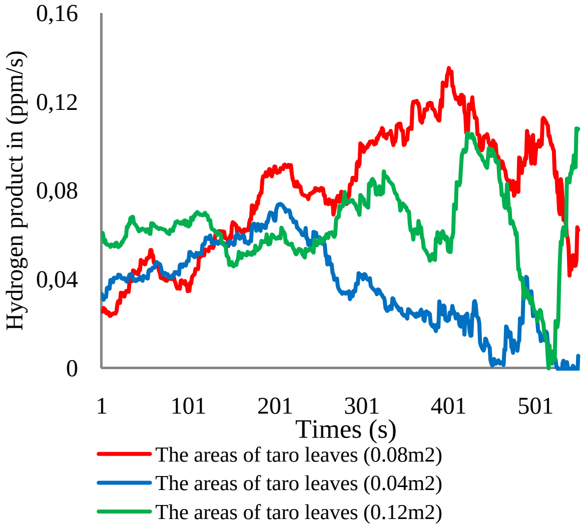


Fig. 13. Hydrogen production in (ppm/s)

IV. Conclusion

This research aims at uncovering the mechanism of gas formation that is trapped or formed within a droplet and at identifying the substance contained in the gas when a water droplet is in contact with taro leaves surface. The mechanism of how the hydrogen gas is formed on taro leaves can be concluded as follows:

a) There is a reaction between water and taro leaves surface at the contact point with papilla. The contact point on the nano sharp points of leaves surface stores a very high surface tension energy triggering a reaction to produce hydrogen gas.
b) The emergence of Brownian motion indicates that the water molecule vibrates more intensively due to the high surface tension of the droplet. The more intense vibration of water molecules triggers a reaction between the elements on taro leaves surface (Ca, Mg, and K) with water producing H_2 gas.
c) There are two gas phenomena forming on the taro leaves surface, which are: gas trapped in the nano spaces and gas emerged in the droplet coming from the gas trapped on the leaves surface. The gas bubbles emerging in the droplet is caused by the pressure exceeding the surface tension of the droplet so that it periodically penetrates the water droplet.

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References

[1] Dean B, Bhushan B, (2010), Shark-skin surfaces for fluid-drag reduction in turbulent flow: A review. *Philosophical Transactions of the Royal Society* A, 2010, 368, 4775–4806.
DOI: 10.1098/rsta.2010.0201

[2] Bhushan, B., (2009), Biomimetics: lesson from nature-an overview, *Phil. Trans. R. Soc.* A (2009) 367, 1445-1486.
DOI: 10.1098/rsta.2009.0011

[3] Bhushan, B., Jung, Y. C. & Koch, K. In press. Micro-, nano-, and hierarchical structures for superhydrophobicity, self-cleaning and low adhesion. *Phil. Trans. R. Soc.* A 367.
DOI: 10.1098/rsta.2009.0014

[4] Koch, K., Bhushan, B., Jung, Y. C. & Barthlott, W. In press b. Fabrication of artificial lotus leavesand significance of hierarchical structure for superhydrophobicity and low adhesion. *Soft Matter*.
DOI: 10.1039/B818940D

[5] Roach, P., Shirtcliffe, N. J. & Newton, M. I. (2008) Progress in superhydrophobic surface development. *Soft Matter* 4, 224–240.
DOI: 10.1039/b712575p

[6] Wang, S., Song, Y. & Jiang, L. (2007) Photoresponsive surfaces with controllable wettability. *J. Photochem. Photobiol. C: Photochem. Rev.* 8, 18–29.
DOI: 10.1016/j.jphotochemrev.2007.03.001

[7] Xia, F., *et al*, (2006) Dual-responsive surfaces that switch between superhydrophilicity and superhydrophobicity. *Adv. Mater.* 18, 432–436.
DOI: 10.1002/adma.200501772

[8] Bhushan, B. & Ling, X. (2008) Integrating electrowetting into micromanipulation of liquid. *J. Phys. Condens. Matter* 20, 485 009.
DOI: 10.1088/0953-8984/20/48/485009

[9] Barthlott, W. and Neinhuis, C., (1997), Purity of the Sacred Lotus, or Escape from Contamination in Biological Surfaces,*Planta* 202 (1997) 1-8.
DOI: 10.1007/s004250050096

[10] Wagner, P., *et al*, (2003), Quantitative Assessment to the Structural Basis of Water Repellency in Natural and Technical Surfaces, *J. Exper. Botany* 54 (2003) 1295-1303.
DOI: 10.1093/jxb/erg127
[11] Burton, Z. and Bhushan, B., (2006), Surface Characterization and Adhesion and Friction Properties of Hydrophobic Leaf Surfaces, *Ultramicroscopy* 106 (2006) 709-719.
DOI: 10.1016/j.ultramic.2005.10.007
[12] Bhushan, B., (2009), Biomimetics: Lessons from Nature – An Overview, *Phil. Trans. R. Soc.* A367 (2009) 1445-1486.
DOI: 10.1098/rsta.2009.0011
[13] Koch, K., Bhushan, B., and Barthlott, W., (2008), Diversity of Structure, Morphology, and Wetting of Plant Surfaces (invited), *Soft Matter 4* (2008a) 1943-1963.
DOI: 10.1039/B804854A
[14] Koch, K., Bhushan, B., and Barthlott, W., (2009), Multifunctional Surface Structures of Plants: An Inspiration for Biomimetics (invited), *Prog. Mater. Sci.* 54 (2009a) 137-178.
DOI: 10.1016/j.pmatsci.2008.07.003
[15] Hans J. Ensikat., *et al.*, (2011), Superhydrophonicity in perfection: the outstanding properties of the lotus leaf, *Beilstein J. Nanotechnol.* 2011,2,152-161.
DOI: 10.3762/bjnano.2.19
[16] R. Blossey, (2003), Self-cleaning surfaces- virtual realities, *Nature Materials*, 2 301 306.
DOI: 10.1038/nmat856
[17] Bhushan, B. dan Jung, Y.C., (2006), Micro and Nanoscale Characteriztion of Hydrophobic and Hydrophilic Leaf Surfase, *Nanotechnology* 17 (2006) 2758-2772.
DOI: http://dx.doi.org/10.1088/0957-4484/17/11/008
[18] Muler, F., *et al*., (2007), Self-Cleaning Surfaces Using the Lotus Effect, in Handbook for Cleaning/Decontamination of Surfaces. 2007, *Elsevier Science* B.V.: Amsterdam. p. 791-811.
[19] Burton, Z. and Bhushan, B., (2005), Hydrophobicity, Adhesion, and Friction Properties of Nanopatterned Polymers and Scale Dependence for Micro- and Nanoelectromechanical Systems, *Nano Lett*. 5 (2005) 1607-1613.
DOI: 10.1021/nl050861b
[20] Koch, K. and H.-J. Ensikat, (2008), The hydrophobic coatings of plant surfaces: Epicuticular wax crystals and their morphologies, crystallinity and molecular self-assembly. *Micron*, 2008. 39(7): p. 759-772.
DOI: 10.1016/j.micron.2007.11.010
[21] Jianwei Ma, (2010), *Impact of surface topography on colloid and bacterial adhesion*, A thesis submitted in partial fulfulment of the requirements for the degree master of science, Rice University, Houston,Texas.
[22] Jiadao Wang., *et al*., (2009), Investigation on hydrophobicity of lotus leaf: Experiment and theory, Plant Science 176 (2009) 687-695.
DOI: 10.1016/j.plantsci.2009.02.013

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