

Microstructures of superhydrophobic plant leaves - inspiration for efficient oil spill cleanup materials

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2016 Bioinspir. Biomim. 11 056003

(<http://iopscience.iop.org/1748-3190/11/5/056003>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 89.216.30.123

This content was downloaded on 17/08/2016 at 10:02

Please note that [terms and conditions apply](#).

You may also be interested in:

[The role of bio-inspired hierarchical structures in wetting](#)

H S Grewal, Il-Joo Cho and Eui-Sung Yoon

[PAN/PS elctrospun fibers for oil spill cleanup](#)

Qiao Ying, Zhao Lili, Sun Haixiang et al.

[The dream of staying clean: lotus and biomimetic surfaces](#)

Andreas Solga, Zdenek Cerman, Boris F Striffler et al.

[Micro-and nanoscale characterization of hydrophobic and hydrophilic leaf surfaces](#)

Bharat Bhushan and Yong Chae Jung

[Effect of the porous structure of polymer foams on the remediation of oil spills](#)

Javier Pinto, Athanassia Athanassiou and Despina Fragouli

[Wetting, adhesion and friction of superhydrophobic and hydrophilic leaves and fabricated micro/nanopatterned surfaces](#)

Bharat Bhushan and Yong Chae Jung

[A fast, precise and low-cost replication technique for nano- and high-aspect-ratio structures](#)

Kerstin Koch, Anna Julia Schulte, Angelika Fischer et al.

Bioinspiration & Biomimetics



PAPER

Microstructures of superhydrophobic plant leaves - inspiration for efficient oil spill cleanup materials

Claudia Zeiger¹, Isabelle C Rodrigues da Silva^{1,3}, Matthias Mail², Maryna N Kavalenka¹, Wilhelm Barthlott² and Hendrik Hölscher¹

¹ Karlsruhe Institute of Technology, Institute of Microstructure Technology, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany

² University of Bonn, Nees Institute for Biodiversity of Plants, Venusbergweg 22, D-53115 Bonn, Germany

³ Present Address: Universidade Federal de Ouro Preto, Campus Morro do Cruzeiro, Ouro Preto—MG, 35400-0000.

E-mail: hendrik.hoelscher@kit.edu

Keywords: *Salvinia*, oil spill cleanup, superhydrophobic, *Pistia*, oil/water separation, environmentally friendly oil sorbents, bioinspiration
Supplementary material for this article is available [online](#)

Abstract

The cleanup of accidental oil spills in water is an enormous challenge; conventional oil sorbents absorb large amounts of water in addition to oil and other cleanup methods can cause secondary pollution. In contrast, fresh leaves of the aquatic ferns *Salvinia* are superhydrophobic and superoleophilic, and can selectively absorb oil while repelling water. These selective wetting properties are optimal for natural oil absorbent applications and bioinspired oil sorbent materials. In this paper we quantify the oil absorption capacity of four *Salvinia* species with different surface structures, water lettuce (*Pistia stratiotes*) and Lotus leaves (*Nelumbo nucifera*), and compare their absorption capacity to artificial oil sorbents. Interestingly, the oil absorption capacities of *Salvinia molesta* and *Pistia stratiotes* leaves are comparable to artificial oil sorbents. Therefore, these pantropical invasive plants, often considered pests, qualify as environmentally friendly materials for oil spill cleanup. Furthermore, we investigated the influence of oil density and viscosity on the oil absorption, and examine how the presence and morphology of trichomes affect the amount of oil absorbed by their surfaces. Specifically, the influence of hair length and shape is analyzed by comparing different hair types ranging from single trichomes of *Salvinia cucullata* to complex eggbeater-shaped trichomes of *Salvinia molesta* to establish a basis for improving artificial bioinspired oil absorbents.

1. Introduction

Today crude oil is an important energy resource and an essential raw material for many state-of-the-art chemical products and processes. The worldwide consumption of oil and petroleum products for 2016 is predicted to be ~94 million barrels per day [1]. Massive oil consumption leads to an increased threat of oil pollution, as oil exploration, transportation, storage, processing and usage activities are all accompanied by the risk of oil spillage [2–4]. As oil pollution has a severe negative impact on the environment and public health, research on novel methods for oil spill cleanup and treatment of oily wastewater has increased in recent years [5–10]. Conventional methods for cleaning oily water, such as chemical dispersion or controlled burning, are potentially toxic or could

cause secondary pollution [2, 11]. Alternatively, selective absorption is the method of choice for removing oil from water. Most sorbents used to collect spilled oil absorb large amounts of water in addition to oil and have limited oil absorption capacity. To overcome these problems, materials with special wetting properties, which repel water while absorbing oil (superhydrophobic/superoleophilic) are required [12–17]. Novel approaches for fabricating such materials focus on polymeric sponges, metal meshes and fabrics modified or coated with metal or metal oxide, nanoparticles or silicon compounds [18–24]. However, many of these technical materials are potentially harmful to the environment during production, usage or disposal, or are economically inefficient [25].

The use of environmental friendly methods inspired by nature or based on biological materials is a

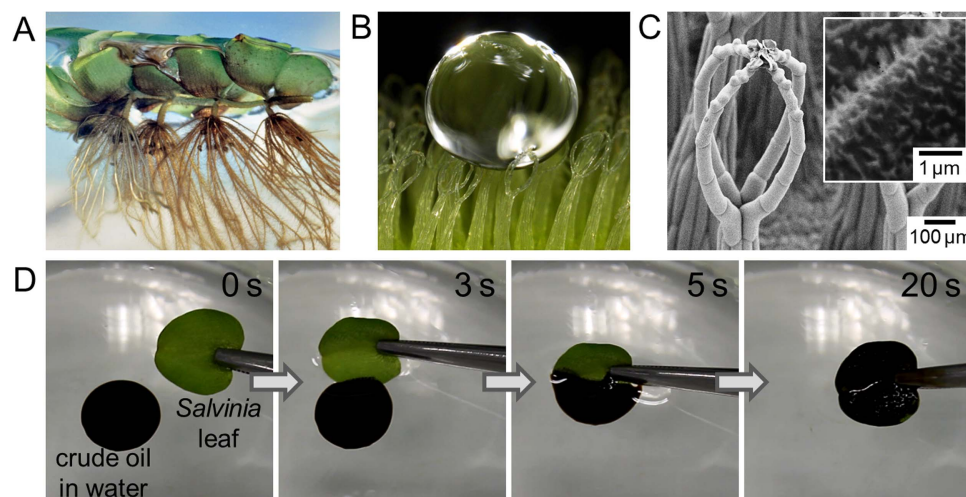


Figure 1. (a) Floating fern *Salvinia molesta* has two types of leaves: brown submerged root-like leaves and green floating leaves. (b) Photograph of a water droplet on eggbeater-shaped superhydrophobic trichomes covering the upper side of floating *Salvinia molesta* leaves. Extreme water repellency of *Salvinia* leaves is caused by the hierarchical structure and hydrophobic wax coverage. (c) SEM images of the three-level hierarchical structure of *S. molesta*, consisting of several hundred micrometers high trichomes, microscale convex cells and nanoscale wax crystals (inset). (d) Demonstration of fast and selective oil absorption by a *S. molesta* floating leaf within 20 s. After dipping a leaf into a simulated oil spill on the water surface, oil is absorbed quickly whereas water is repelled by the superhydrophobic hairy structures on the upper side of the leaf (see supplemental video).

promising approach in the search for a solution for effective oil/water separation [12, 26–29]. Biological materials commonly used for oil spill cleanup, such as saw dust, wheat straw, milkweed fibers or aquatic plants, however, absorb both oil and water [7, 13, 30–36]. In contrast, the aquatic floating weeds *Salvinia molesta* and *Pistia stratiotes* gained interest as selective oil sorbents due to their superhydrophobic trichome-covered surface [32, 33, 35, 36]. Superhydrophobicity as a feature of many biological surfaces occurs from the combination of hydrophobic surface chemistry (e.g. wax) and hierarchical micro- and nanoscaled surface structure. Surface coverage with hydrophobic wax protects plants from excessive water evaporation, microorganisms, mechanical damage or degradation by water [37]. Lotus leaves gain superhydrophobic and self-cleaning properties from their two-level hierarchical surface structure (microbumps formed by convex papillae, covered by nanoscale wax crystals). *Salvinia* (see figure 1) and *Pistia* leaves have a more complex three-level hierarchical surface architecture. Their trichomes (hairs) are several hundred microns high, and contain microscale convex cells superimposed with nanoscale wax crystals [12, 38]. In addition to water repellency, the trichome-covered leaves retain a stable air layer on their surface, which ensures buoyancy and survival of the plant when dragged underwater [39].

The water-repelling properties of the floating fern *Salvinia* and its ability to retain an air layer underwater have been examined for other technical applications such as fluid drag reduction and water harvesting [27, 38, 40–43]. *Salvinia molesta* and *Pistia stratiotes* originate from South America and spread throughout the tropical and subtropical parts of the world where

they proliferate and became a pest [44–49]. These pest plants found in abundance in nature are potential candidates to be used not only for removal of inorganic contaminants such as heavy metals, nitrate and phosphate from water [50, 51], but also as natural oil sorbents. The latter is due to a combination of water repellency, increased surface wetting with low surface tension liquids such as oils, and capillary action in the interstices between trichomes. It has been previously shown that dried powdered leaves of *S. molesta* and *P. stratiotes* can serve as oil sorbents [32, 35, 36]. But dry powdered leaves with desiccated surface structures lose their superhydrophobicity and, similarly to other biological materials, absorb significant amounts of water. The effect of hierarchical hairs (trichomes) on the water repellency of leaves is well known [41, 52], but the influence of the trichomes on the oil absorption capacity of the leaves, to the best of our knowledge, has not yet been investigated. An interesting example of the oil absorption by hairy structures in nature is oil-collecting bees, which use energy-rich floral oil for larval nutrition. With their hair-covered legs and abdomen these highly specialized bees successfully collect large amounts of oil from oil flowers [53–55]. Therefore, we assume that the hierarchical hairy surface structures of *Salvinia* and *Pistia* leaves play a key role not only in the superhydrophobicity of the plant leaves, but also in their ability to absorb oil.

In this study, we investigate the efficiency of the whole leaves of *Salvinia* and other plants for oil absorption. First, we study how the physical properties of oil, such as density and viscosity, influence the sorption capacity of *Salvinia molesta* leaves. Next, the oil absorption capacities of fresh and dry leaves of superhydrophobic plants *Salvinia molesta*, *Pistia stratiotes*

(water lettuce) and *Nelumbo nucifera* (Lotus) are investigated to reveal the influence of the leaf surface structure on oil absorption. Furthermore, the oil absorption efficiency of the plant leaves is compared to that of synthetic oil sorbents. Finally, we study the oil sorption capacity of four *Salvinia* species (*S. molesta*, *S. oblongifolia*, *S. minima* and *S. cucullata*), comparing the four different trichome types found in the genus. Thus we explore the physical aspects of oil absorption by hairy surface architectures to investigate the influences of hair morphology and size on oil absorption. Our study both identifies plants which have a great potential to be used as natural sorbents for selective absorption of spilled oil from water and provides a basis for improving bioinspired artificial hairy oil absorbers [26, 27].

2. Methods

Salvinia molesta (BG BONN 14459), *Salvinia oblongifolia* (BG BONN 14457), *Salvinia minima* (BG BONN 8595), *Salvinia cucullata* (BG BONN 18268), *Nelumbo nucifera* (BG BONN 14404) and *Pistia stratiotes* (BG BONN 1077) plants were provided by the Botanical Gardens of the University of Bonn. Fresh leaves from living plants were washed with tap water and used for the measurements immediately. For oil sorption experiments of *Salvinia* we used only their floating leaves (i.e. no root-like submerged leaves). The keel-like aerenchyma was removed from *S. oblongifolia*. To produce vacuum-dried leaves, the leaves were washed with tap water and dried in vacuum at room temperature for 24 h. For CPD-dried *S. molesta* leaves, leaves were dehydrated through a graded ethanol series (50%–100% ethanol) and subsequently dried in a critical point drier (CPD 020, Balzers Union, Lichtenstein). The oil sorption capacity was quantified in two ways: per area in g m^{-2} (oil/leaf surface) and per weight in mg/mg (oil/leaves).

To determine the surface area of leaves they were flattened by a glass slide, photographed on graph paper, and the corresponding area was measured by analyzing the photos with image processing software [56]. As *Pistia stratiotes* leaves are covered with trichomes on the upper and lower sides of the leaves, the measured surface area values for *Pistia* were doubled. The samples were weighed and then immersed into oil for 30 s. The subsequent draining of the leaves by suspension (90s) was used to remove excessive oil, and the drained leaves were weighed again. The difference in weight before and after immersing in oil was determined as amount of absorbed oil. Four different oils were used: artificial crude oil (Grüssing Roherdölersatz PAE15805, $\rho = 0.805 \text{ g ml}^{-1}$, $\nu \approx 4 \text{ mm}^2 \text{ s}^{-1}$), hydraulic oil (Total Azolla ZS 10, $\rho = 0.839 \text{ g ml}^{-1}$, $\nu \approx 21 \text{ mm}^2 \text{ s}^{-1}$) and two types of crude oil (MiRO OK 679, $\rho = 0.856 \text{ g ml}^{-1}$, $\nu \approx 6 \text{ mm}^2 \text{ s}^{-1}$ and MiRO

EK 651, $\rho = 0.878 \text{ g ml}^{-1}$, $\nu \approx 30 \text{ mm}^2 \text{ s}^{-1}$, Mineraloelraffinerie Oberrhein, Germany). When not otherwise stated, hydraulic oil (Total Azolla ZS 10) is used for oil absorption experiments. We also measured the sorption capacity of commercial oil sorbents (Öl-Ex Allwetter Typ III R [57] and Deurex Pure [58] with hydraulic oil, following the same procedure as for the leaves.

3. Results and discussion

To achieve efficient oil spill cleanup on water by selective oil absorption, the absorbing material has to repel water and absorb oil. This prerequisite is perfectly fulfilled by the floating leaves of the water fern *Salvinia*. They are superhydrophobic and retain an air layer under water due to their surface architecture and wax coverage (figure 1) [40, 41, 59, 60]. To demonstrate the capability of *Salvinia* for separating oil from water, we dipped *Salvinia molesta* floating leaves into a simulated crude oil spill as shown in figure 1(d) and supplemental video. *Salvinia* leaves selectively absorb oil from water within seconds due to the combination of superhydrophobic and superoleophilic properties. After less than 30 s the maximum absorption is reached and the oil is retained by the leaves till the plant material starts to degrade after some days (figure S1). These basic experiments are the first indication of the great potential of *S. molesta* floating leaves as selective oil absorber.

To test the efficiency of *Salvinia* leaves as oil sorbents, explain the mechanism of oil absorption by different trichome structures and find an optimal absorbing architecture, we quantify the absorption capacity of *Salvinia* species and other plants. First, we measured the sorption capacity of *Salvinia molesta* leaves (g m^{-2}) with four different oils in order to study the influence of physical oil properties on the absorption capacity. Artificial crude oil (PAE15805, number of sample leaves $n = 10$), hydraulic oil (Total Azolla ZS 10, $n = 10$), and two types of crude oil (MiRO OK 679 and MiRO EK 651, $n = 5$ leaves each) were used for these measurements. The results depicted in figure 2 indicate that higher oil density leads to higher oil absorption capacity. For better comparison of the measured values, the influence of the oil density on the measurement was eliminated by converting the values from g m^{-2} to ml m^{-2} : *Salvinia molesta* absorbs on average 630.0 ml m^{-2} of artificial crude oil, 774.8 ml m^{-2} of hydraulic oil, 989.3 ml m^{-2} of crude oil OK 679 and 1099.6 ml m^{-2} of crude oil EK 651. As artificial crude oil has lowest viscosity and EK 651 the highest, it can also be deduced that higher oil viscosity can lead to higher oil uptake (see figure S2). Though hydraulic oil is more viscous than crude oil OK 679, the crude oil consists of multiple chemical components which might influence the absorption and result in higher oil absorption capacity values. In general,

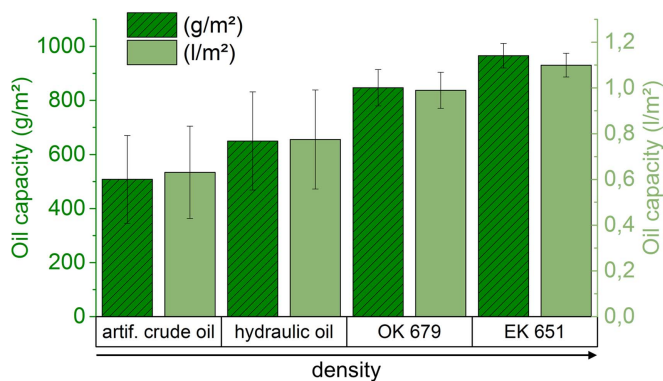


Figure 2. Oil absorption capacity per leaf surface of *Salvinia molesta* (fresh floating leaves), measured for four different oils: artificial crude oil, hydraulic oil and two types of crude oil (OK 679 and EK 651). The oil density increase is marked with an arrow, with artificial crude oil having the lowest density. In order to eliminate the possible influence of the oil density on the measurement, oil absorption (g m^{-2}) was also converted to l m^{-2} .

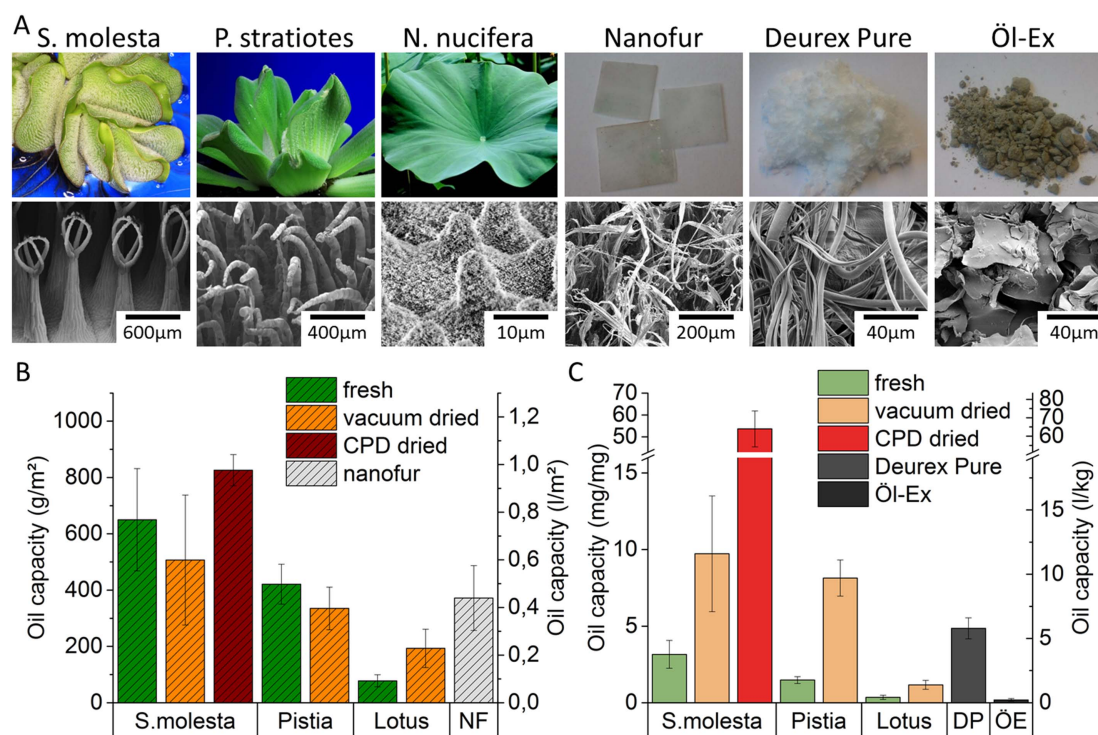


Figure 3. Comparison between different oil sorbents and their oil absorption capacity. (a) Photos and SEM images of tested sorbents: leaves of *Salvinia molesta*, *Pistia stratiotes* and *Nelumbo nucifera* (Lotus) and artificial sorbents nanofur, Deurex Pure and Öl-Ex. (b) Hydraulic oil absorption capacity per leaf surface of fresh and dried *Salvinia molesta*, *Pistia stratiotes* and *Nelumbo nucifera* leaves. Fresh and vacuum dried leaves of all plants were used, and additionally *Salvinia molesta* leaves were dried in a critical point dryer (CPD). The typical oil capacity of nanofur is shown on the right in this graph. (c) Oil absorption capacity per weight of fresh and dried *Salvinia molesta*, *Nelumbo nucifera* and *Pistia stratiotes* leaves, and of two commercial oil sorbents (Deurex Pure and Öl-Ex).

these results show that *Salvinia* absorbs and retains different types of oil, and that its sorption capacity depends on the physical properties of the oil used.

The importance of the ‘hair-type’ structures (trichomes) on the leaf surface for effective oil absorption can be observed by comparing absorption of trichome-covered leaves (with intact trichomes and trichomes desiccated by drying) with non-hairy plant leaves. Photos and SEM images of sorbents and their structures are shown in figure 3(a), and include

complex hairy *Salvinia molesta* leaves, simple hairy leaves of *Pistia stratiotes*, papillate leaves of *Nelumbo nucifera* and tested artificial sorbents. The oil absorption capacities measured on fresh and vacuum-dried hairy *Salvinia molesta* and *Pistia stratiotes* are compared to the capacity of non-hairy *Nelumbo nucifera* leaves covered with hierarchical wax structures in figures 3(b) and (c) (number of samples: $n = 14$ (vacuum-dried *Salvinia*), $n = 10$ (fresh *Salvinia*, CPD-dried *Salvinia* and fresh and dry *Nelumbo*

nucifera), $n = 3$ (*Pistia stratiotes* and all artificial sorbents)). The results shown in figure 3(b) indicate that both fresh and vacuum-dried *Salvinia molesta* and *Pistia stratiotes* absorb more oil per area (g m^{-2}) than *Nelumbo nucifera* leaves. For dry plant leaves, there is absorption within the inner tissue of the plants (bulk material) in addition to absorption by surface structure. This explains the higher absorption of CPD dried *Salvinia molesta* leaves compared with fresh leaves. When *S. molesta* and *P. stratiotes* leaves are dried in vacuum, the trichomes become partially deformed and wrinkled, whereas they are perfectly conserved when CPD dried. This results in lower absorption capacity (g m^{-2}) of the vacuum-dried leaves, and emphasizes the importance of the trichomes on the leaf surface for the high oil uptake.

The oil absorption capacities of both plants with trichomes (*Pistia stratiotes* and *Salvinia molesta*) are similar in uptake per m^2 , but *P. stratiotes* has a lower capacity per weight (mg/mg) as its leaves are thicker and heavier than *S. molesta* leaves (figure 3(c)). In general, dry leaves of all plants tested absorb more oil than fresh ones, which is a result of lower weight after water loss (e.g. the weight loss of *Salvinia molesta* through drying is $\sim 87\%$). Together with the high absorption by the surface structure and bulk material, this leads to CPD-dried *Salvinia molesta* leaves having an order of magnitude higher sorption capacity compared to other samples.

We compared the oil absorption capacities of plants to two commercial oil sorbents (Deurex Pure and Öl-Ex) and polymeric hair-covered nanofur [27]. Comparable to leaves with trichomes, the artificial oil sorbents with hair-like morphology (Deurex Pure and nanofur) absorb a larger amount of oil than the non-hairy sorbent (Öl-Ex) (see figure 3). In general, the comparison shown in figure 3 indicates that hairy superhydrophobic structures (*Salvinia molesta* and *Pistia stratiotes*), where capillary interstices between trichomes are available for oil absorption, absorb significantly more oil than non-hairy papillate superhydrophobic structures (*Nelumbo nucifera*). Additionally, the deformation of trichomes reduces the oil absorption capacity. This result proves that the trichomes (hairs) play a key role not only in the special wetting properties of the leaves, but also in increasing their oil absorption capability.

Dry leaves of both *Salvinia molesta* and *Pistia stratiotes* have higher oil absorption capacity than the commercial synthetic oil sorbents tested here. Consequently, they have a great potential to be used as natural oil sorbents, which are biodegradable. Air-dried leaves have similar properties as vacuum-dried samples, enabling cost-effective drying of leaves in large amounts. For selective oil absorption from oil/water mixtures, however, dry leaves of *Salvinia* are inefficient as only the dorsal side of leaves, which is covered with trichomes shows superhydrophobic properties when dry. The ventral side of dry *Salvinia* leaves

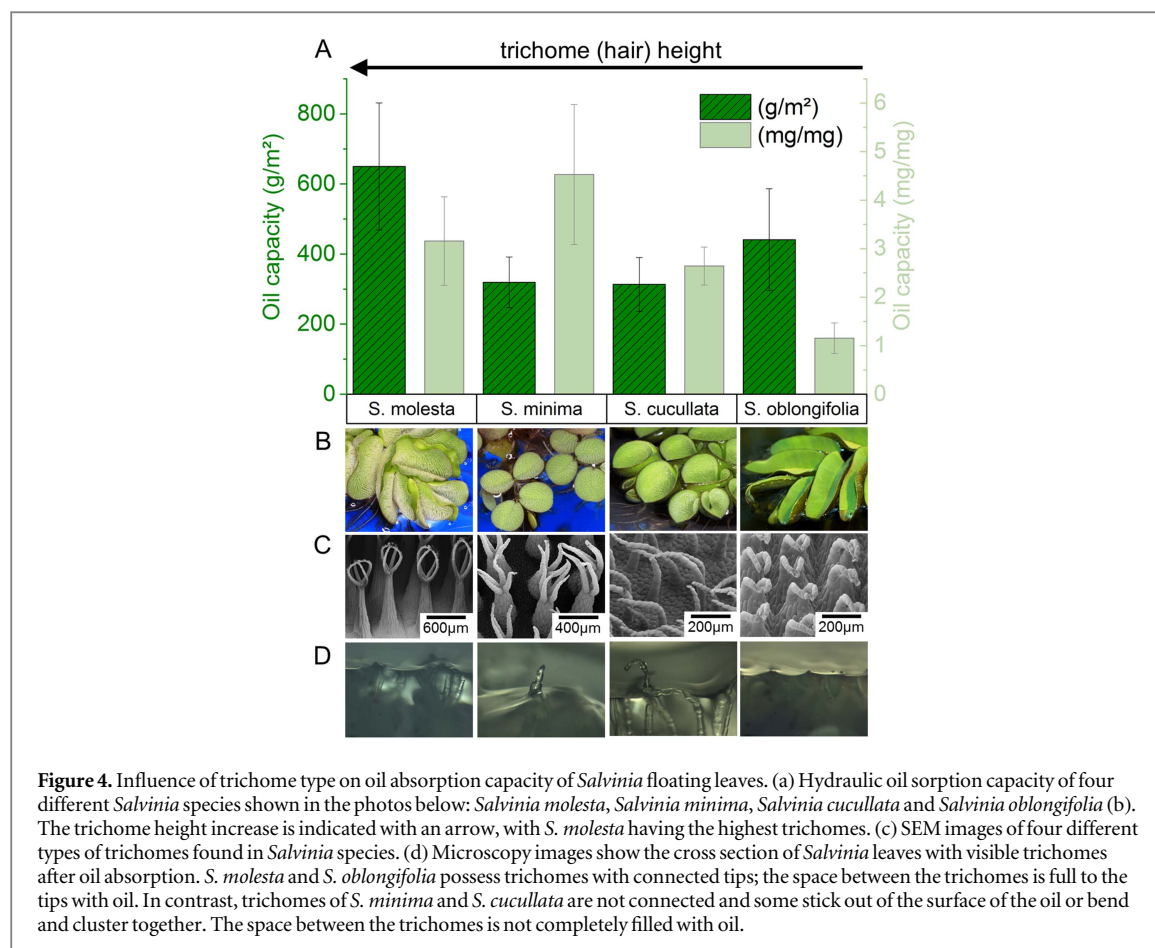
however absorbs water, which significantly increases the weight of waste to be disposed and drastically decreases economic efficiency. Dried leaves of *Pistia stratiotes*, in contrast, remain water repellent as both sides of the leaves are covered with superhydrophobic trichomes. This is advantageous for oil/water separation compared to *Salvinia*.

To investigate the influence of the particular trichome morphology on the oil absorption capacity of leaves, we tested different *Salvinia* species (*S. molesta*, *S. minima*, *S. cucullata* and *S. oblongifolia*) possessing trichomes with different shapes [40, 59]. All *Salvinia* species have a complex hierarchical three-level leaf surface architecture, providing trichomes consisting of convex cells with superimposed wax crystals [38]. The structural parameters of different types of *Salvinia* trichomes are summarized in table 1, and SEM images of the trichomes are shown in figure 4(c). Solitary single-standing Cucullata type trichomes are slightly bent and on average are $558 \mu\text{m}$ high. On *Salvinia minima*, trichomes of Natans type form groups of four and are $\sim 919 \mu\text{m}$ high. Oblongifolia type trichomes are bent in the same direction and the terminal ends of two trichomes are connected. With an average height of $310 \mu\text{m}$, they are shorter than the other types. Molesta type trichomes are the highest trichomes with a height of $\sim 2629 \mu\text{m}$, on which groups of four trichomes with fused ends, sitting on one emergence, form an eggbeater-like shape [39]. The comparison of oil absorption by fresh leaves of *S. molesta*, *S. minima*, *S. cucullata* and *S. oblongifolia* is shown in figure 4(a). *Salvinia molesta* has highest sorption capacity per leaf surface and absorbs 650 g m^{-2} of oil, *S. oblongifolia* absorbs 441.1 g m^{-2} oil, *S. cucullata* and *S. minima* absorb 313.5 g m^{-2} and 319.3 g m^{-2} (table 1). Number of samples was $n = 7$ for *S. minima* and $n = 10$ for all other species.

Mayser et al [39] measured the volume of air retained by the hairy structures of different *Salvinia* types when submerged under water, and showed that *S. molesta* retains the largest air volume per surface area and *S. oblongifolia* the smallest, as they have longest and shortest trichomes compared to other *Salvinia* species. For oil absorption capacity (figure 4(a)), trichome height also plays a key role, as *S. molesta* both has the longest trichomes and highest oil sorption capacity. But contrary to our expectations, the trichome height and volume available between the trichomes are not the only crucial criteria determining the sorption capacity. *Salvinia oblongifolia* has the second highest oil sorption capacity per area, while its hairs are the shortest of all four species (figures 4(b), (c) and table 1), and it has lowest air volume [39]. As the oil absorption by *Salvinia* species does not exclusively correlate with the trichome height or the cavity volume between the trichomes, we also studied the influence of trichome architecture on the absorption. The common characteristic of the two species with highest oil sorption (*S. molesta* and *S. oblongifolia*) is

Table 1. Comparison of four different *Salvinia* species: trichome height and type, leaf size and normalized mass, oil absorption capacity. For absorption capacity measurements, fresh floating *Salvinia* leaves were used, the keel-like aerenchyma was removed from *S. oblongifolia*.

	<i>S. molesta</i>	<i>S. minima</i>	<i>S. cucullata</i>	<i>S. oblongifolia</i>
Typical trichome height, μm from [39]	2629 $\pm$ 285	919 $\pm$ 107	558 $\pm$ 143	310 $\pm$ 41
Trichome type from [40]	Molesta type: groups of four sitting on one emergence, ends fused, egg-beater shape	Natans type: groups of four sitting on one emergence, ends separated	Cucullata type: solitary trichomes	Oblongifolia type: groups of two, ends connected
Leaf size, mm^2	256 $\pm$ 73	23 $\pm$ 3	156 $\pm$ 31	543 $\pm$ 178
Leaf mass per area, g m^{-2}	207 $\pm$ 18	76 $\pm$ 30	118 $\pm$ 17	387 $\pm$ 95
Oil capacity, g m^{-2}	650.0 $\pm$ 181.4	319.3 $\pm$ 72.6	313.5 $\pm$ 76.9	441.1 $\pm$ 145.5
Oil capacity, mg mg^{-1}	3.2 $\pm$ 0.9	4.5 $\pm$ 1.4	2.6 $\pm$ 0.4	1.2 $\pm$ 0.3



that the ends of their trichomes are connected, as can be seen from SEM images in figure 4(c). In contrast, the trichomes of the other two species with lower capacity are separated.

The conclusion that fusion of the tips of the trichomes increases the absorption and retention of oil, is additionally supported by the microscopy images of the leaf cross sections after oil absorption shown in figure 4(d). The trichomes of *S. minima* and *S. cucullata* bend, cluster together or stick out from the oil after oil absorption, which decreases the volume available for oil sorption in two ways. First, when the surface area of a single standing trichome touching the oil/air interface is too small and surface tension of the oil is too low to provide an oil/air interface which can be supported by the trichome tip, the tip breaks through the interface and the volume available for retaining oil is reduced by the part of the trichome sticking out. This phenomenon was commonly observed in *S. minima* trichomes, which have highest stiffness per trichome group of all trichome types [61], and occasionally observed in more elastic *S. cucullata* trichomes. On the other hand, single bent trichomes provide a larger surface area touching the oil/air interface, and do not break through the surface. But in this case the volume available for retaining oil is reduced due to the reduced height of bent trichomes. In particular, trichomes of *S. cucullata* have lowest stiffness of

all trichome types [61], which leads to significantly decreased oil sorption capacity due to trichome bending. In contrast, the complex shape and lower elasticity of the connected trichomes of *S. molesta* and *S. oblongifolia* lead to upright-standing trichomes with only the terminal trichome ends being bent. It prevents a decrease in trichome height resulting in a decrease of volume available for oil absorption, and ensures that a large surface area of the trichome tip touches the oil/air interface, providing a proper interface support. As a result, spaces between trichomes of *S. molesta* and *S. oblongifolia* can serve as oil retaining space over the entire trichome height, whereas the volume available for retaining oil between trichomes of *S. minima* and *S. cucullata* is decreased.

Fabricating hierarchical artificial hairy structures for absorbing oil, which are inspired by these results, would allow achieving higher oil sorption capacity. Oleophilic and hydrophobic surface chemistry and the hierarchical nature of the micro- and nanostructured hairs with capillary interstices ensure effective and selective oil absorption. Intuitively and as a result from our studies, long hairs provide higher sorption capacities than short hairs. However the hair length is not the only crucial factor; additionally, the ends of rigid hairs should be connected and/or bent down to ensure the oil/air interface is supported and the spaces between the hairs are available for oil absorption,

resulting in high oil absorption capacity. In the case of non-connected straight hairs, inelastic hairs provide no support for the oil/air interface, whereas extreme deformation occurs when elasticity of hairs is high. In both cases the oil absorption capacity is decreased. In contrast, moderate elasticity of hairs or rigid hairs with elastic tips ensure appropriate bending of hairs and, therefore, high oil absorption capacity.

4. Conclusion

The leaves of the invasive and fast growing floating plants *Salvinia molesta* and *Pistia stratiotes* achieve superhydrophobic properties through their complex hierarchical surface structure and can be used to selectively absorb oil spilled in water. We demonstrated that *Salvinia molesta* absorbs oil within seconds with a sorption capacity dependent on the physical properties of the oil. When used for oil absorption from oil/water mixtures, fresh leaves are water repellent and can selectively absorb oil. Dry *Salvinia* leaves, however, are only hydrophobic on the trichome-covered top side of the leaves, and the bottom side absorbs water in addition to oil. In contrast, dry leaves of *Pistia stratiotes* are water-repellent when dry, as both sides are covered with trichomes. We compared the oil capacity of *Salvinia molesta* leaves to *Pistia stratiotes* and *Nelumbo nucifera* and our results revealed that complex hierarchically structured hairy superhydrophobic surfaces of *Salvinia molesta* and *Pistia stratiotes* leaves absorb more oil than simpler structured papillate superhydrophobic surfaces of *Nelumbo nucifera* leaves. In addition, we investigated the influence of trichome morphology on oil absorption by comparing oil uptake of different *Salvinia* species (*S. molesta*, *S. minima*, *S. cucullata* and *S. oblongifolia*). Contrary to the intuitive assumption, we discovered that not only the trichome height plays a role in oil absorption capacity, but also the architecture of trichomes. We showed that due to larger volume available for oil absorption *Salvinia* species with fused trichomes (*S. molesta* and *S. oblongifolia*) achieve higher oil sorption capacities than those with separated trichomes (*S. cucullata* and *S. minima*). It follows that artificial oil sorbents can benefit from having a hair-like complex hierarchical surface as it combines superhydrophobic properties of hierarchical surface architectures, and high oil sorption capacity of hairy structures. For achieving high absorption capacity, hairs should not only be long, but also feature bent and/or fused tips to ensure the oil/water interface is supported and spaces between the hairs can fill to the tip with oil. Our study confirms that living organisms have developed in more than 420 million years of evolution the most complex and sophisticated mechanisms for the interaction with liquids [62] for biomimetic technical applications.

Acknowledgments

It is a pleasure to thank Paul Abaffy, Markus Guttmann and Richard Thelen for their support and help in the lab. The Botanical Gardens of the University of Bonn kindly provided *Salvinia*, *Pistia stratiotes* and *Nelumbo nucifera* plants. We thank MiRO Mineraloelraffinerie Oberrhein GmbH & Co. KG for the crude oil and viscosity measurements; and Steffen Remdt for the samples of DEUREX Pure. This work was carried out in part with the support of the Carl Zeiss Foundation, the Brazilian research and exchange program Ciências sem Fronteiras (Science Without Borders) and the Karlsruhe Nano Micro Facility (KNMF, www.kit.edu/KNMF), a Helmholtz Research Infrastructure at Karlsruhe Institute of Technology (KIT, www.kit.edu).

References

- [1] 'EIA—Energy Information Administration,' [Online]. Available: (eia.gov). (Accessed 20 12 2015)
- [2] Whitfield J 2003 How to clean a beach *Nature* **422** 464–6
- [3] MacDonald I R, Kammen D M and Fan M 2014 Science in the aftermath: investigations of the DWH hydrocarbon discharge *Environ. Res. Lett.* **9** 125006.
- [4] Boufadel M C and Geng X 2014 A new paradigm in oil spill modeling for decision making? *Environ. Res. Lett.* **9** 081001
- [5] Fingas M 2012 *The Basis of Oil Spill Cleanup* 3rd edn (Boca Raton, FL: CRC Press)
- [6] Cornwall W 2015 Deepwater Horizon: after the oil *Science* **348** 22–9
- [7] Wahi R, Chuah L, Choong T, Ngaini Z and Nourouzi M 2013 Oil removal from aqueous state by natural fibrous sorbent: an overview *Sep. Purif. Technol.* **113** 51–63
- [8] Liu Z, Liu J, Zhu Q and Wu W 2012 The weathering of oil after the Deepwater Horizon oil spill: insights from the chemical composition of the oil from the sea surface, salt Marshes and sediments *Environ. Res. Lett.* **7** 035302
- [9] McClenachan G, Turner R E and Tweel A W 2013 Effects of oil on the rate and trajectory of Louisiana Marsh shoreline erosion *Environ. Res. Lett.* **8** 044030
- [10] Carassou L, Hernandez F J and Graham W M 2014 Change and recovery of coastal mesozooplankton community structure during the Deepwater Horizon oil spill *Environ. Res. Lett.* **9** 124003
- [11] Prince R C 2015 Oil spill dispersants: boon or bane? *Environ. Sci. Technol.* **49** 6376–84
- [12] Bhushan B 2016 *Biomimetics—Bioinspired Hierarchical-structured Surfaces for Green Science and Technology* 2nd edn (Switzerland: Springer)
- [13] Choh H M and Cloud R M 1992 Natural sorbents in oil spill cleanup *Environ. Sci. Technol.* **26** 772–6
- [14] Feng L, Zhang Z, Mai Z, Ma Y, Liu B, Jiang L and Zhu D 2004 A superhydrophobic and super oleophilic coating mesh film for the separation of oil and water *Angew. Chem.* **116** 2046–8
- [15] Tuteja A, Choi W, Ma M, Mabry J M, Mazzella S A, Rutledge G C, McKinley G H and Cohen R E 2007 Designing superoleophobic surfaces *Science* **318** 1618–22
- [16] Brown P S and Bhushan B 2007 Bioinspired, roughness-induced, water and oil super-philic and super-phobic coatings prepared by adaptable layer-by-layer technique *Sci. Rep.* **5** 14030
- [17] Solga A, Cerman Z, Striffler B F, Spaeth M and Barthlott W 2007 The dream of staying clean: lotus and biomimetic surfaces *Bioinspir. Biomim.* **2** 126–34
- [18] Wang B, Li J, Wang G, Liang W, Zhang Y, Shi L, Guo Z and Liu W 2013 Methodology for robust superhydrophobic fabrics and sponges from in situ growth of transition metal/metal

- oxide nanocrystals with thiol modification and their applications in oil/water separation *ACS Appl. Mater. Interfaces* **5** 1827–39
- [19] Zhu Q, Pan Q and Liu F 2011 Facile removal and collection of oils from water surfaces through superhydrophobic and superoleophilic sponges *J. Phys. Chem. C* **115** 17464–70
- [20] Wu J, Chen J, Qasim K, Xia J, Lei W and Wang B P 2012 A hierarchical mesh film with superhydrophobic and superoleophilic properties for oil and water separation *J. Chem. Technol. Biotechnol.* **87** 427–30
- [21] Wang C, Yao T, Wu J, Ma C, Fan Z, Wang Z, Cheng Y, Lin Q and Yang B 2009 Facile approach in fabricating superhydrophobic and superoleophilic surface for water and oil mixture separation *ACS Appl. Mater. Interfaces* **1** 2613–7
- [22] Deng D, Prendergast D P, MacFarlane J, Bagatin R, Stellacci F and Gschwend P M 2013 Hydrophobic meshes for oil spill recovery devices *ACS Appl. Mater. Interfaces* **5** 774–81
- [23] Zhang J and Seeger S 2011 Polyester materials with superwetting silicone nanofilaments for oil/water separation and selective oil absorption *Adv. Funct. Mater.* **21** 4699–704
- [24] Sabir S 2015 Approach of cost-effective adsorbents for oil removal from oily water *Crit. Rev. Environ. Sci. Technol.* **45** 1916–45
- [25] Wu L, Zhang J, Li B and Wang A 2014 Mechanical- and oil-durable superhydrophobic polyester materials for selective oil absorption and oil/water separation *J. Colloid Interface Sci.* **413** 112–7
- [26] Kavalenka M N, Hopf A, Schneider M, Worgull M and Hölscher H 2014 Wood-based microhaired superhydrophobic and underwater superoleophobic surfaces for oil/water separation *RSC Adv.* **4** 31079–83
- [27] Röhrig M, Mail M, Schneider M, Louvin H, Hopf A, Schimmel T, Worgull M and Hölscher H 2014 Nanofur for biomimetic applications *Adv. Mater. Interfaces* **1** 130083
- [28] Korhonen J T, Kettunen M, Ras R H A and Ikkala O 2011 Hydrophobic nanocellulose aerogels as floating, sustainable, reusable, and recyclable oil absorbents *ACS Appl. Mater. Interfaces* **3** 1813–6
- [29] Yang H-C, Liao K-J, Huang H, Wu Q-Y, Wan L-S and Xu Z-K 2014 Mussel-inspired modification of a polymer membrane for ultra-high water permeability and oil-in-water emulsion separation *J. Mater. Chem. A* **2** 10225–30
- [30] Annunziato T R, Sydenstricker T H D and Amico S C 2005 Experimental investigation of various vegetable fibers as sorbent materials for oil spills *Mar. Pollut. Bull.* **50** 1340–6
- [31] Li D, Zhu F Z, Li J Y, Na P and Wang N 2012 Preparation and characterization of cellulose fibers from corn straw as natural oil sorbents *Ind. Eng. Chem. Res.* **52** 516–24
- [32] Yang X, Chen S and Zhang R 2014 Utilization of two invasive free-floating aquatic plants (*Pistia stratiotes* and *Eichhornia crassipes*) as sorbents for oil removal *Environ. Sci. Pollut. Res.* **21** 781–6
- [33] Abd-Elnaby A M and Egorov M A 2012 Efficiency of different particle sizes of dried *Salvinia natans* in the removing of Cu(II) and oil pollutions from water *J. Water Chem. Technol.* **34** 143–6
- [34] Sánchez-Galván G, Mercado F J and Olguín E J 2013 Leaves and roots of *Pistia stratiotes* as sorbent materials for the removal of crude oil from saline solutions *Water Air Soil Pollut.* **224** 1421
- [35] Ribeiro T H, Rubio J and Smith R W 2003 A dried hydrophobic aquaphyte as an oil filter for oil/water emulsions *Spill Sci. Technol. B* **8** 483–9
- [36] Ribeiro T H, Smith R W and Rubio J 2000 Sorption of oils by the nonliving biomass of a *Salvinia* sp *Environ. Sci. Technol.* **34** 5201–5
- [37] Witka-Jeżewska E and Hupka J 2003 Investigation of oleophilic nature of straw sorbent conditioned in water *Spill Sci. Technol. Bull.* **8** 561–4
- [38] Koch K and Barthlott W 2009 Superhydrophobic and superhydrophilic plant surfaces: an inspiration for biomimetic materials *Phil. Trans. R. Soc. A* **367** 1487–509
- [39] Mayser M J, Bohn H F, Reker M and Barthlott W 2014 Measuring air layer volumes retained by submerged floating-ferns *Salvinia* and biomimetic superhydrophobic surfaces *Beilstein J. Nanotechnol.* **5** 812–21
- [40] Barthlott W, Wiersch S, Čolić Z and Koch K 2009 Classification of trichome types within species of the water fern *Salvinia*, and ontogeny of the egg-beater trichomes *Botany* **87** 830–6
- [41] Barthlott W et al 2010 The *Salvinia* paradox: superhydrophobic surfaces with hydrophilic pins for air retention under water *Adv. Mater.* **22** 2325–8
- [42] Kavalenka M N, Vüllers F, Lischker S, Zeiger C, Hopf A, Röhrig M, Rapp B E, Worgull M and Hölscher H 2015 Bioinspired air-retaining nanofur for drag reduction *ACS Appl. Mater. Interface* **7** 10651–10655
- [43] Azad M, Barthlott W and Koch K 2015 Hierarchical surface architecture of plants as an inspiration for biomimetic fog collectors *Langmuir* **31** 13172–9
- [44] Pimentel D 2002 *Encyclopedia of Pest Management* (New York: CRC Press)
- [45] Room P M, Harley K L S, Forno I W and Sands D P A 1981 Successful biological control of the floating weed *Salvinia* *Nature* **294** 78–80
- [46] Jacono C and Pitman B 2001 *Salvinia molesta*: around the world in 70 years *Aquatic Nuisance Species Dig.* **4** 13–6
- [47] Chikwenhere G P 1994 Biological control of water lettuce in various impoundments of Zimbabwe *J. Aquat. Plant Manage.* **32** 27–9
- [48] Abbasi S A and Nipanay P C 1991 Biogas production from the aquatic weed *Pistia* (*Pistia stratiotes*) *Bioresour. Technol.* **37** 211–4
- [49] Mbati G and Neuenschwander P 2005 Biological control of three floating water weeds, *Eichhornia crassipes*, *Pistia stratiotes*, and *Salvinia molesta* in the Republic of Congo *BioControl* **50** 635–45
- [50] de Moraes Ferreira R, de Souza M D P, Takase I and de Araujo Stapelfeldt D M 2016 Pb(II) adsorption by biomass from chemically modified aquatic macrophytes, *Salvinia* sp. and *Pistia stratiotes* *Water Sci. Technol.* **73** 2670–79
- [51] Dhir B 2013 *Phytoremediation: Role of Aquatic Plants in Environmental Clean-Up* (Berlin: Springer)
- [52] Grewal H S, Cho I-J and Yoon E-S 2015 The role of bio-inspired hierarchical structures in wetting *Bioinspir. Biomim.* **10** 026009
- [53] Vogel S 1981 Abdominal oil-mopping—a new type of foraging in bees *Naturwissenschaften* **68** 627–8
- [54] Buchmann S L 1987 The ecology of oil flowers and thier bees *Ann. Rev. Ecol. Syst.* **18** 343–69
- [55] Rüttgers A, Griebel M, Pastrik L, Schmied H, Wittmann D, Scherrieble A, Dinkelmann A and Stegmaier T 2015 Simulation of the oil storage process in the scopa of specialized bees *Comput. Fluids* **119** 115–30
- [56] 'ImageJ,' [Online]. Available: (<http://imagej.net>)
- [57] 'puren® GmbH,' [Online]. Available: (puren.com/industrie/oel-e)
- [58] 'Deurex®,' [Online]. Available: (deurex.com/en)
- [59] Cerman Z, Striffler B F and Barthlott W 2009 Dry in the water: the superhydrophobic water fern *Salvinia*—a model for biomimetic in functional surfaces *Functional Surfaces in Biology—Little Structures with Big Effects* ed S N Gorb (Heidelberg: Springer) pp 97–111
- [60] Yang C-Y, Yang C-Y and Sung C-K 2013 Enhancing air retention by biomimicking *Salvinia molesta* structures *Japan. J. Appl. Phys.* **52** 06GF08
- [61] Ditsche P, Gorb E, Mayser M, Gorb S, Schimmel T and Barthlott W 2015 Elasticity of the hair cover in air-retaining *Salvinia* surfaces *Appl. Phys. A* **121** 505–11
- [62] Barthlott W, Mail M and Neinhuis C 2016 Superhydrophobic hierarchically structured surfaces in biology: evolution, structural principles and biomimetic applications *Phil. Trans. R. Soc. A* **374** 20160191