Superhydrophobic and superhydrophilic plant surfaces: an inspiration for biomimetic materials

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The diversity of plant surface structures, evolved over 460 million years, has led to a large variety of highly adapted functional structures. The plant cuticle provides structural and chemical modifications for surface wetting, ranging from superhydrophilic to super-hydrophobic. In this paper, the structural basics of superhydrophobic and superhydrophilic plant surfaces and their biological functions are introduced. Wetting in plants is influenced by the sculptures of the cells and by the fine structure of the surfaces, such as folding of the cuticle, or by epicuticular waxes. Hierarchical structures in plant surfaces are shown and further types of plant surface structuring leading to superhydrophobicity and super-hydrophilicity are presented. The existing and potential uses of superhydrophobic and superhydrophilic surfaces for self-cleaning, drag reduction during moving in water, capillary liquid transport and other biomimetic materials are shown.

Keywords: hierarchical structures; superhydrophobic; superhydrophilic; self-cleaning; lotus effect; biomimetic

1. Introduction

Biological surfaces provide a large diversity of structures and capabilities, such as self-healing and self-assembly. Their structural diversity and properties evolved over several millions of years by a long-lasting game of mutation and selection. Adaptations to different environments led to a huge structural variety and the development of multifunctional, protective interfaces. Their properties are desirable for a wide variety of artificial biologically inspired materials. Prominent examples of biomimetic materials, whose properties are based on surface characters, are water-repellent and self-cleaning materials fabricated after the biological model of lotus leaves (Forbes 2008; Genzer & Marmur 2008) and surfaces that reduce drag during movement in water, such as the skin of sharks (Bechert *et al.* 2000).

The diversity of plant surface structures is based on the variability of cell shapes, micro- and nanostructures on the cell surfaces, and by the formation of multicellular structures. Based on these cellular and subcellular units, a nearly
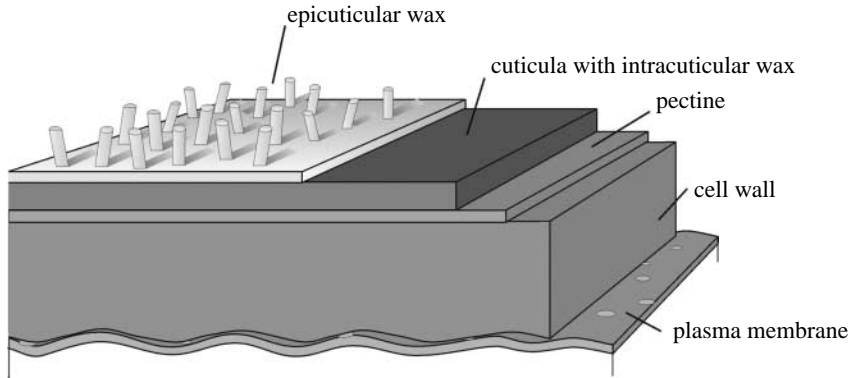
Figure 1. A simplified model of the stratification of the outermost layers of the plant epidermal cells. The epicuticular wax layer is shown in its most common form, as a composite of three-dimensional waxes and an underlying wax film. The cuticle with its integrated waxes is connected with the underlying cellulose wall by pectin, here simply visualized as a layer. Below the cell wall, the plasma membrane is shown. It separates the water-containing part of the cell from the outermost structure forming components of the epidermis above.

unlimited combination of structures leads to the large existing structural diversity and functional surfaces in plants (Koch *et al.* 2008*a*, 2009). Surface properties in plants include the provision of mechanical stability (Bargel *et al.* 2006), provision of an efficient water transpiration barrier and minimizing the leaching of molecules from the inside of the living cells (Kerstiens 1996*a*,*b*; Riederer & Müller 2006). Structure-related properties of plant surfaces include the formation of low-adhesive surfaces, e.g. sliding of insects (Gorb *et al.* 2005), and an increase in the reflection of visible light or absorption of harmful UV radiation (Barnes & Cardoso-Vilhena 1996; Pfündel *et al.* 2006). Structures of plant surfaces are also relevant for surface wettability. Within the last decade, a lot of attention has been given to the superhydrophobic and self-cleaning properties of plant surfaces, but in plants also water-spreading (superhydrophilic) surfaces and all stages of wettability in between superhydrophobic and superhydrophilic can be found. Wetting of surfaces is related to surface structuring and surface chemistry; thus in the following, these are briefly introduced.

The epidermal cells represent the outermost cell layer of all primary plant surfaces, e.g. leaves, petals, fruits and herbaceous stems. A simplified model of the epidermal cell stratification is presented in figure 1. The outermost layer of the epidermis is the cuticle. The cuticle covers nearly all aerial tissues of land-living plants as a continuous extracellular membrane, but is absent in roots and secondary tissues. One of the most important attributes of the cuticle is its function as a transpiration barrier (Riederer & Schreiber 2001). The cuticle is basically composed of a polyester called cutin, and integrated (intracuticular) and superimposed (epicuticular) waxes (Holloway 1994). The epicuticular waxes play an important role in surface structuring at a subcellular scale, and are introduced later in detail. The cuticle network is formed by cutin and sometimes also by cutan or by another polymer called lignin (Kolattukudy 2001; Jeffree 2006). The next layer, shown in figure 1, is the pectin layer. Pectin is the overall term for different complex polysaccharides that connect the cuticle to the much

thicker underlying cellulose wall. The last layer shown is the plasma membrane, which separates the living compartment of the water-containing cell from the outer non-living part of the epidermis.

(*a*) *Micro- and nanostructures of plant surfaces*

(i) *The microstructures of plant surfaces*

The basic unit for surface structuring is the single epidermal cell. The micromorphology of plant surfaces is formed by the outline and sculpture of a single epidermal cell. The primary sculpture encompasses the outline, including the shape and relief of the anticlinal walls (two perpendicular cell walls) and curvature of the outer periclinal wall (outer area of the cell). The basic cell curvatures are tabular (flat), convex (arced to the outside) and concave (arced to the inside), whereby the most common cell shape is the convex form. According to their shape and aspect ratio (height to width ratio), convex cells can be divided into several subtypes, such as hemisphere, cupola, cone, papilla, hair papilla and hair (Koch *et al.* 2008*a*). Epidermal cells with an aspect ratio of 7:1 or higher are called hairs or trichomes (Greek: trichoma). The diversity of hair morphology and their functions have been reviewed by Wagner *et al.* (2004). In plants, hairs can also be composed of several cells (multicellular hairs), and examples and their significance in surface wetting will be introduced later.

(ii) *The structures of cell surfaces*

In plants, two kinds of cell surface structuring are common: epicuticular waxes and cuticular patterns. The latter are induced by cuticle folding or subcuticular inserts, whereas the epicuticular waxes are superimposed structures on the cuticle.

Epicuticular waxes are sometimes visible as a white or bluish coloration of leaves and fruits, such as grapes and plums. These colorations are induced by the reflection of part of the visible light spectrum by a dense coverage of three-dimensional wax structures (Müller & Riederer 2005). But, even when there is not a bluish coloration visible, three-dimensional waxes can be present in lower amounts, or in the form of smooth, thin films. Plant waxes are mixtures of aliphatic and cyclic hydrocarbons and their derivatives, and several reviews have addressed the chemical composition of plant waxes (Kunst & Samuels 2003; Jeffree 2006; Jetter *et al.* 2006). The chemical composition of plant waxes is highly variable among plant species, the organs of one species (e.g. different leaves) and during organ ontogeny (Jeffree 2006; Jetter *et al.* 2006). Nearly all the existing data on the chemical composition of plant waxes are based on solvent-extracted waxes. These are mixtures of epicuticular and intracuticular waxes, which may be chemically different (Jetter & Schäffer 2001; Wen *et al.* 2007). The epicuticular waxes are crystalline (Reynhardt & Riederer 1994; Dorset 1997, 1999; Schreiber *et al.* 1997; Ensikat *et al.* 2006) and occur in different morphologies ranging in sizes from 0.2 to 100 µm. Overviews about the terminology and micromorphology of epicuticular waxes are given by Barthlott *et al.* (1998) and Jeffree (2006). Based on the chemical and morphological features and the consideration of the orientation of single wax crystals on the surface, Barthlott *et al.* (1998) introduced 23 different wax types and subtypes. Jeffree (2006) distinguished six main morphological wax types, but suggested

many more subtypes, based on the chemical differences found, e.g. for wax tubules. The most common wax morphologies shown in figure 2 are films (*Hydrocotyle bonariensis*; figure 2a), crusts (*Crassula ovata*; figure 2b), β-diketone tubules (*Eucalyptus gunnii*; figure 2c), nonacosan-ol tubules (*Thalictrum flavum glaucum*; figure 2d), platelets (*Robinia pseudoacacia*; figure 2e), rodlets (*Brassica oleracea*; figure 2f) and transversely ridged rodlets (*Sassafras albidum*; figure 2g). Scanning electron microscopy (SEM) investigations of plant material do not illustrate the composite structure of three-dimensional waxes with an underlying wax film. Therefore, a simple mechanical isolation method has been used to transfer the epicuticular waxes onto a smooth artificial surface (Ensikat *et al.* 2000). Figure 2h shows waxes isolated from a leaf of *Tropaeolum majus* on a glass surface, and the edges of the underlying film and, on top, three-dimensional wax tubules are visible.

Recrystallization experiments with isolated waxes showed that the different wax morphologies arise by self-assembly (Jeffree *et al.* 1975; Jetter & Riederer 1994). In these studies, most of the investigated waxes recrystallized in the same morphology as found on the plant surface. The self-assembly process of waxes has been studied by atomic force microscopy (AFM; Koch *et al.* 2004). AFM combines sufficient resolving power to image nanostructures with the ability to work at standard temperature and pressure (STP) with living plant material.

The second type of cell surface structure originates by the structuring of the cuticle. Such cuticular patterns have been described for nearly all above-ground surfaces of plants, but are very frequently found in the leaves of flowers (petals) and on seed surfaces. They occur as folding or tubercular (verrucate) patterns that originate due to the cuticle itself, by the expression of the bulk of the cell wall below, or by subcuticular inserts (Barthlott & Ehler 1977).

Subcuticular inserts can be silicon dioxide crystals, as shown in figure 3a,b for the shoots and leaves of the horsetail (*Equisetum arvense*). Silicon (Si) is a bioactive element associated with beneficial effects on mechanical and physiological properties of plants (Sangster *et al.* 2001). Cuticle folding is shown in figure 3c for the leaves of *Schismatoglottis neoguinensis*. Here, the folding is orderless and covers the complete cell surface. On the lower side (adaxial) of a leaf of *Alocasia macrorhiza*, shown in figure 3d, the cuticle forms node-like folding in the central part of each cell. A high magnification SEM micrograph of the seed surface of *Aztekium ritteri*, shown in figure 3e,f, demonstrates that the origin of surface folding is caused by the cuticle itself. Figure 4 shows the structuring of a cell surface, which can be divided into an inner part, called the central field, and an outer part, called the anticline field. A schematic and a biological example (*Matucana weberbaueri*), shown in figure 4, demonstrate the structural difference within a cell surface.

(b) *Classification of surface wetting*

Wetting is the fundamental process of liquid interaction at solid–gas interfaces. It describes how a liquid comes in contact with a solid surface. The basics of surface wetting are summarized here. For a more in-depth study, specific literature such as the books of Israelachvili (1992), De Gennes *et al.* (2004) and Bhushan (2008) are recommended.
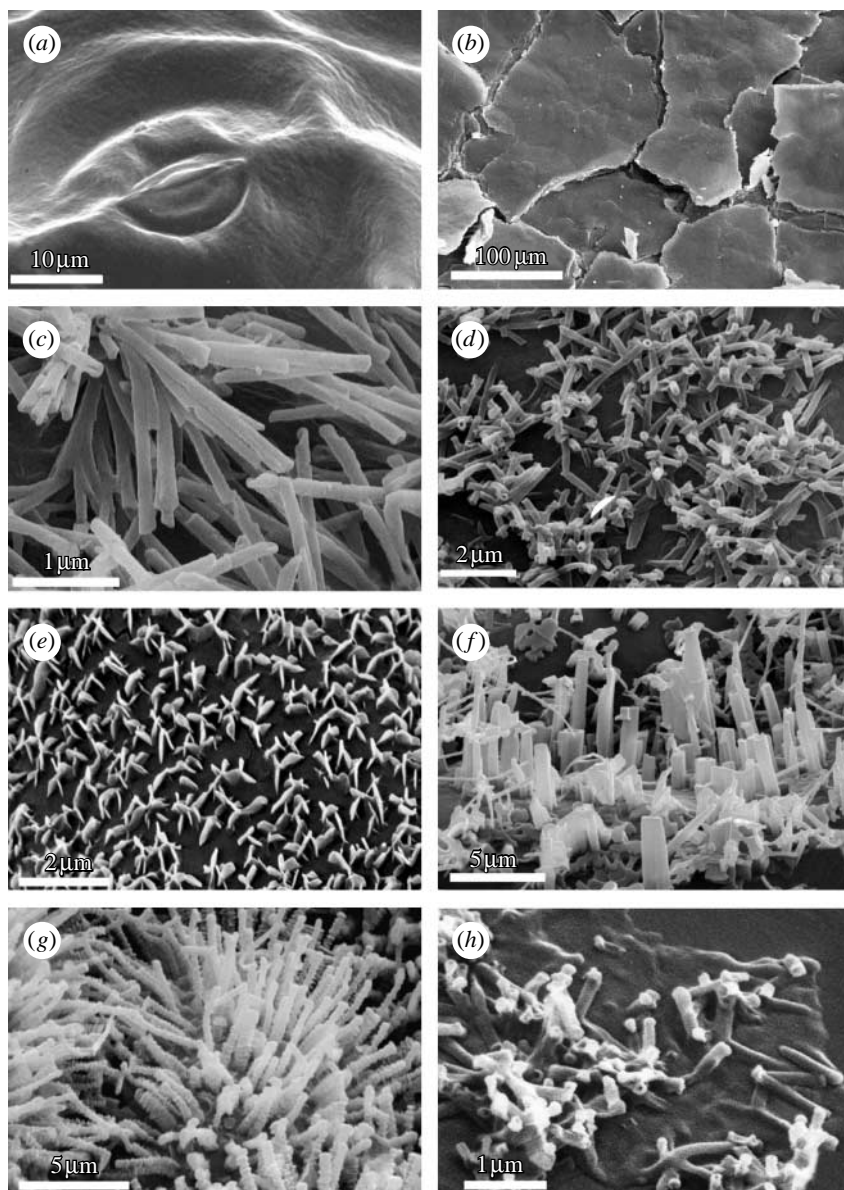
Figure 2. SEM micrographs of cell surface structuring by epicuticular waxes. (*a*) Thin wax films, hardly visible in SEM, cover many plant surfaces as indicated here in *H. bonariensis*. (*b*) A wax crust with fissures on a leaf of *Crassula ovate*, (*c*) β-diketone wax tubules of *E. gunnii* and (*d*) nonacosan-ol tubules on *Thalictrum flavum glaucum* leaves are shown. (*e*) Wax platelets on *Robinia pseudoacacia* leaves are arranged in rosettes. The waxes shown are (*f*) simple rodlets on a leaf of *Brassica oleracea*, whereas the rodlets shown are (*g*) transversely ridged rodlets on a leaf of *Sassafras albidum*. (*h*) Mechanically isolated waxes from a leaf of *Thalictrum flavum* on a glass surface show wax tubules and the underlying wax film.

Contact angle (CA) measurement is the main method for the characterization of the wettability of surfaces, and the CA is the unit for the surface wettability. A high CA describes surfaces on which a water droplet forms a spherical shape,
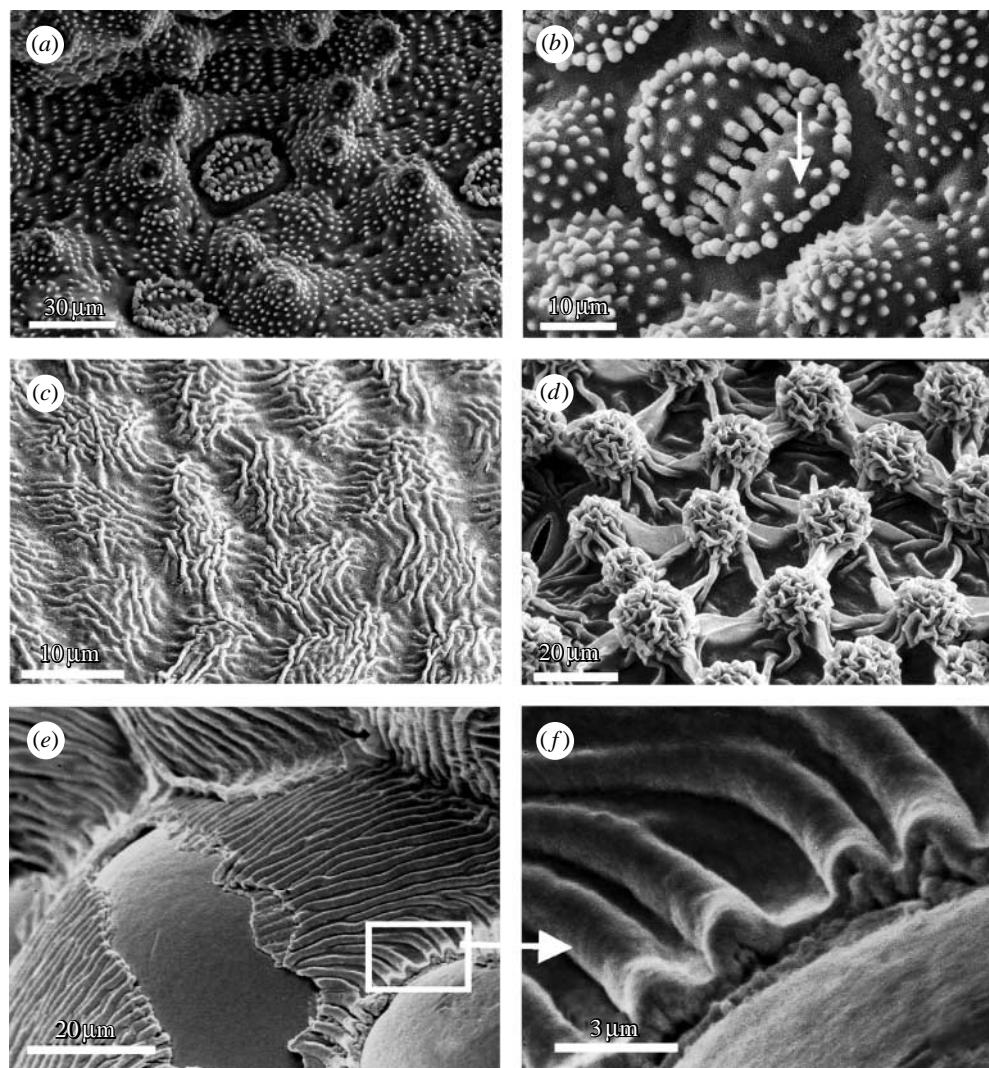
Figure 3. SEM micrographs of cell surface structuring by subcuticular insertions and cuticle folding. (*a*,*b*) The cell surface roughness of the common horsetail, *Equisetum arvensis*, is induced by subcuticular Si-ox inserts (arrow in (*b*)). (*c*) In the leaves of *Schismatoglottis neoguinensis*, the structure of the cell surface is caused by cuticle folding. Here, an irregular cuticular folding is shown, which is restricted to the central field of the cells. (*d*) In *Alocasia macrorhiza*, the cells are flat (tabular), and the cuticle in the central field forms node-like exposed structures (lower leaf side is shown). (*e*,*f*) In *Aztekium ritteri*, a part of the cuticle has been removed to show that surface structuring is induced by the cuticle and not by the underlying cell wall (*f*) shown in detail.

and the real contact between the adhering droplet and the surface is very small. Wettable surfaces, on which an applied drop of water tends to spread, have a low CA. The CA of a liquid on a surface depends on the surface tension (molecular forces) of the involved liquid, the solid surface and the surrounding vapour. Thus, wetting depends on the ratio between the energy necessary for the enlargement of the surface and the gain of energy due to
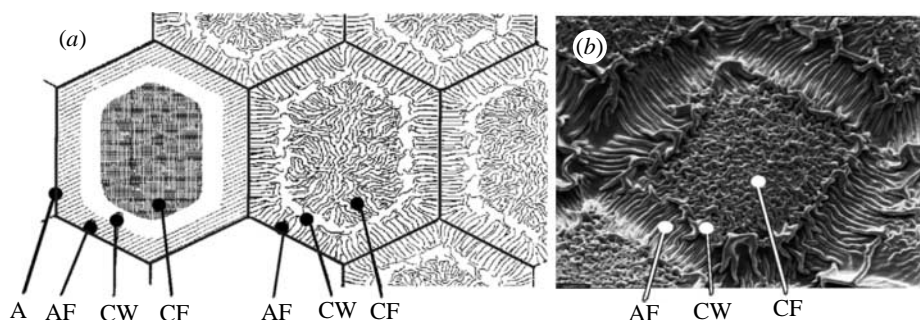
Figure 4. (*a*) A schematic and (*b*) SEM micrograph of *M. weberbaueri* (seed surface) show the structural division and variability of a single cell surface. Anticlines (A) and the directly connected cell area, called the anticline field (AF). The central wall (CW) delimits the central field (CF) in the middle of the cell surface (adapted from Barthlott & Ehler 1977).

adsorption (Adamson 1990; Israelachvili 1992). On water-repellent surfaces, an applied droplet starts to roll off the surface when it is tilted to a specific angle. This tilt angle (TA) is simply defined as the tilting angle of a surface on which an applied drop of water starts to move (Extrand 2002). A TA less than 10° is characteristic for superhydrophobic and self-cleaning surfaces. Another important factor in surface wetting is the hysteresis. Hysteresis is responsible for the sticking of liquids to a surface, and is defined as the difference of the advancing (CA_{adv}) and receding (CA_{rec}) angles of a moving or evaporating, respectively, water-absorbing droplet ($CAH = CA_{adv} - CA_{rec}$). If additional liquid is added to a sessile drop, the contact line advances; if liquid is removed from the drop, the CA decreases to a receding value before the contact retreats. If a droplet moves over a solid surface, the CA at the front of the droplet (advancing CA) is greater than that at the back of the droplet (receding CA). However, if the droplet rolls with little resistance, at a low TA, the CA hysteresis (CAH) is small (Israelachvili 1992).

The basics for studying equilibrium wetting on rough surfaces was established many years ago by Wenzel (1936) and Cassie & Baxter (1944). The Wenzel equation expresses a general amplification of the wettability induced by roughness and applies to a CA where droplets are in equilibrium, but not to advancing and receding angles of a droplet on a rough solid surface, which give rise to CAH.

The wetting behaviour of solid surfaces can be divided into four classes, defined by their static CA and as shown in figure 5. Surfaces are termed superhydrophilic when the CA is less than 10°. Surfaces with CAs more than 10° and less than 90° are termed hydrophilic. Hydrophobic surfaces have high CAs, which means that the liquid on the surface forms a semi-spherical or spherical droplet, and the CA is more than 90° and less than 150°. A superhydrophobic surface has a static CA of more than 150°, and, if those superhydrophobic surfaces have a low hysteresis or a low tilting angle of less than 10°, they are superhydrophobic and can provide self-cleaning properties. The definition of superhydrophobic surfaces given here has been used in most recent reviews (Bhushan & Jung 2007; Jung & Bhushan 2008; Roach *et al.* 2008; Zhang *et al.* 2008), and is used here to overcome the existing varieties of definitions.
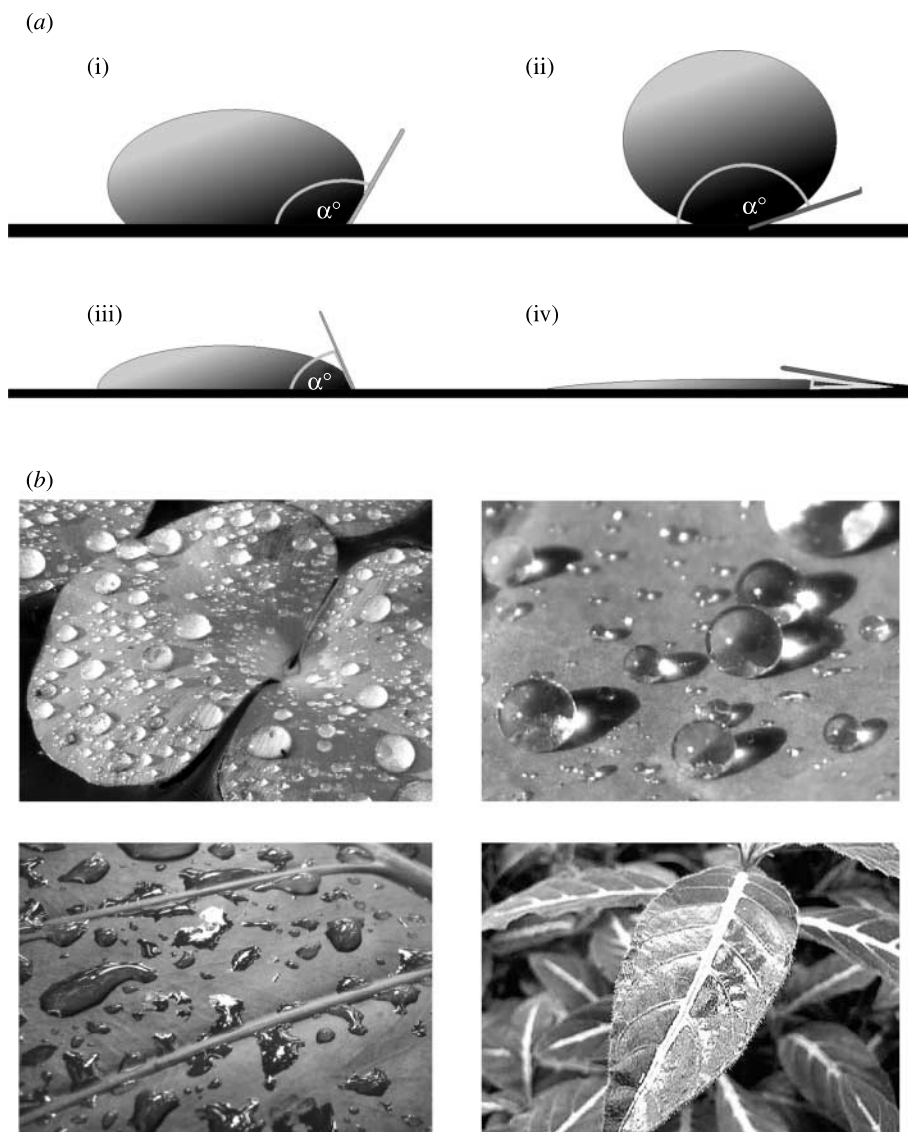
(*a*)

(i)   (ii)

$\alpha°$ $\alpha°$

(iii)   (iv)

$\alpha°$

(*b*)

Figure 5. Four classes of surface wettability, (*a*(i)–(iv)) their characteristic static CAs and (*b*(i)–(iv)) representative leaves are shown. (i) As an example for hydrophobic leaves, *Regnellidium diphyllum* (Marsileaceae) is shown. (ii) A superhydrophobic leaf surface is represented by the leaves of *Brassica oleracea*. (iii) The hydrophilic leaf is *Alocasia odora* and (iv) the superhydrophilic one is *Ruellia devosiana*. (*a*) (i) CA 90–150°, (ii) CA > 150°, (iii) CA > 10° < 90°, (iv) CA < 10°.

2. Superhydrophobicity plant surfaces

(*a*) *Structures for superhydrophobicity and self-cleaning*

The first general remarks about the coherence of plant surface structure and chemistry and their wetting behaviour are given in the early works of Holloway (1969, 1970, 1971). Several data about the surface wettability of leaves of single

species exist in literature, but only a few publications present a general overview of a larger number of species (Martin & Juniper 1970; Rentschler 1971; Hall & Burke 1974). Neinhuis & Barthlott (1997) investigated the surface structures of over 200 water-repellent plant species, and concluded that most of them showed hierarchical surface structures, formed by convex to papillose epidermal cells and a very dense arrangement of three-dimensional epicuticular waxes of different shapes. Several plant surfaces have multiple-length-scale roughness, formed by hairs, convex or papillose epidermal cells, and superimposed three-dimensional waxes (Neinhuis & Barthlott 1997; Herminghaus 2000; Wagner *et al.* 2003; Fürstner *et al.* 2005). Examples of superhydrophobic hierarchical surfaces are the leaves of *Leymus* (*Elymus*) *arenarius* (static CA 161°), with convex cell shapes and wax tubules and the taro plant *Colocasia esculenta* (static CA 164°), with papillose cell shapes and wax platelets.

Superhydrophobicity and self-cleaning of lotus leaves was found to be a result of an intrinsic hierarchical surface structure built by randomly oriented small hydrophobic wax tubules on the top of convex cell papillae (Barthlott & Neinhuis 1997). Wetting of such hierarchical surfaces is minimized, because air is trapped in the cavities of the convex cell sculptures, and the hierarchical roughness enlarges the water–air interface while the solid–water interface is reduced (Bhushan & Jung 2008). Water on such a surface gains very little energy through absorption and forms a spherical droplet, and both the contact area and the adhesion to the surface are dramatically reduced (Extrand 2005; Bhushan & Jung 2008; Li & Amirfaz 2008; Nosonovsky & Bhushan 2008*a*).

Superhydrophobicity in combination with a low hysteresis can lead to self-cleaning properties. The ability of self-cleaning of plant surfaces has been studied in detail for the large shield-formed leaves of the sacred lotus plant (*Nelumbo nucifera*; Barthlott & Neinhuis 1997). The leaves of lotus have a static CA of 162° and are anti-adhesive with respect to particulate contaminations. A particle on such a structured surface is similar to a fakir on his bed of nails, and the contact area and physical adhesion forces between a particle and the underlying leaf surface is considerably reduced. The leaves have a low CAH, and water rolls over such a hydrophobic surface at TAs of 4°. During rolling, contaminating particles are picked up by the water droplets, or they adhere to the surface of the droplets and are then removed with the droplets as they roll off (figure 6*a*). The corresponding surface structure is shown in the SEM micrograph in figure 6*b*. The particle affinity to the water droplets can be explained by the existence of weak van der Waals forces between the particle and the surface (Chow 2007) and much stronger capillary forces between the particle and an adhering water droplet (Pitois & Chateau 2002; Reyssat *et al.* 2008).

It has also been found that tabular (flat) cells with a dense arrangement of wax crystals form superhydrophobic surfaces. One example is the leaves of cabbage (*B. oleracea*), shown in figure 5. However, for these surfaces, the damage of the waxes by environmental influences can result in a less hydrophobic surface in mature leaves.

Additionally, hairy leaf surfaces, such as those on the leaves of the lady's mantle (*Alchemilla vulgaris L.*), are efficiently water repellent. On such surfaces, a deposited drop bends the fibres (hairs), but the stiffness of the hairs prevents contact with the substrate, and promotes a fakir state of the water
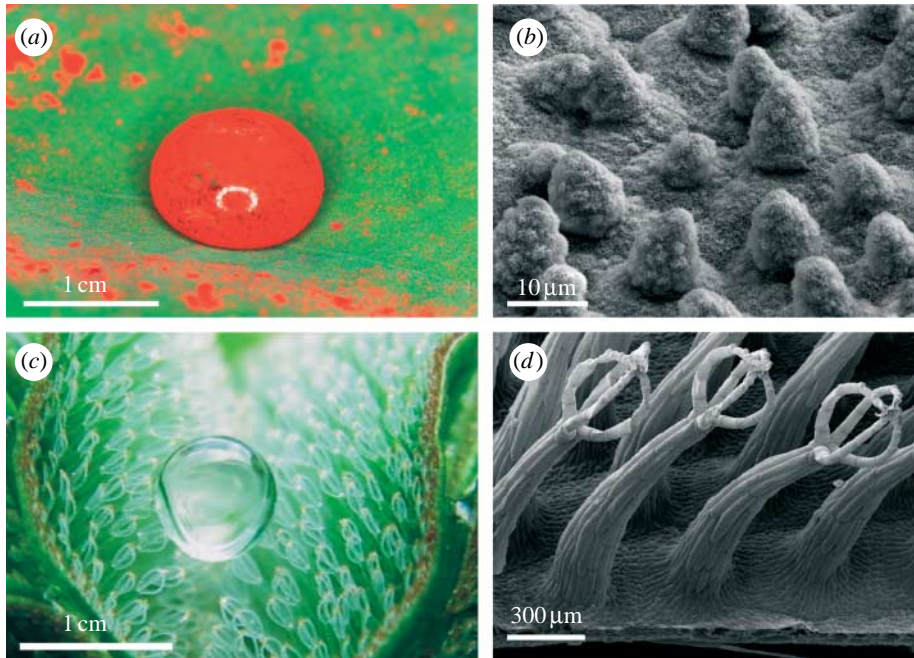
Figure 6. (*a,b*) Superhydrophobic and self-cleaning leaves of lotus (*Nelumbo nucifera*) and (*c,d*) the superhydrophobic and air-retaining leaves of the water fern *Salvinia biloba*. In (*a*) the lotus leaf has been contaminated with Sudan red; a water droplet rolling over the surface collects these lipoidic contaminations. (*c*) The microstructure of the lotus leaf, with its papilla cells and a dense covering of epicuticular wax tubules, is shown. A water droplet on the upper leaf side of *S. biloba* is also shown. (*d*) The large hairs on the leaves of the water fern genus *Salvinia* are multicellular and form a crown-like structure, shown in the SEM micrograph.

droplet (Otten & Herminghaus 2004). Leaves with waxy trichomes are extremely water repellent, as for example on the leaves of *Salvinia auriculata* and *Pistia stratiotes*. The crucial factor of superhydrophobicity in *Salvinia* leaves is given by the hairs, several hundreds of micrometres high, which are superimposed by a layer of small hydrophobic wax crystals (figure 6*c,d*). Cerman *et al.* (2009) showed that the *Salvinia* surfaces are able to retain an air film for up to 17 days when positioned under water. These surfaces are superhydrophobic, but the water droplets do not penetrate between the hairs; thus, small particles from the leaf surface would not be removed by rinsing with water. Superhydrophobic hairy surface structures are also known from animals, such as water beetles and the water spider (Genzer & Marmur 2008). Such hairy systems may also be extremely useful for underwater systems because they minimize the wetted area of immersed surfaces and therefore may greatly reduce drag, as well as the rate of biofilm formation, and are of great interest in biomimetics.

In summary, we can conclude that superhydrophobicity in plants is caused by two-level hierarchical surface structuring formed by papillose cell sculptures with smaller superimposed three-dimensional waxes, as shown in figure 7*a* for lotus (*Nelumbo nucifera*) and in figure 7*b* for *Euphorbia myrsinites*. Superhydrophobic hairy surfaces, such as in *Salvinia*, shown in figure 7*c–e*, provide a three-level
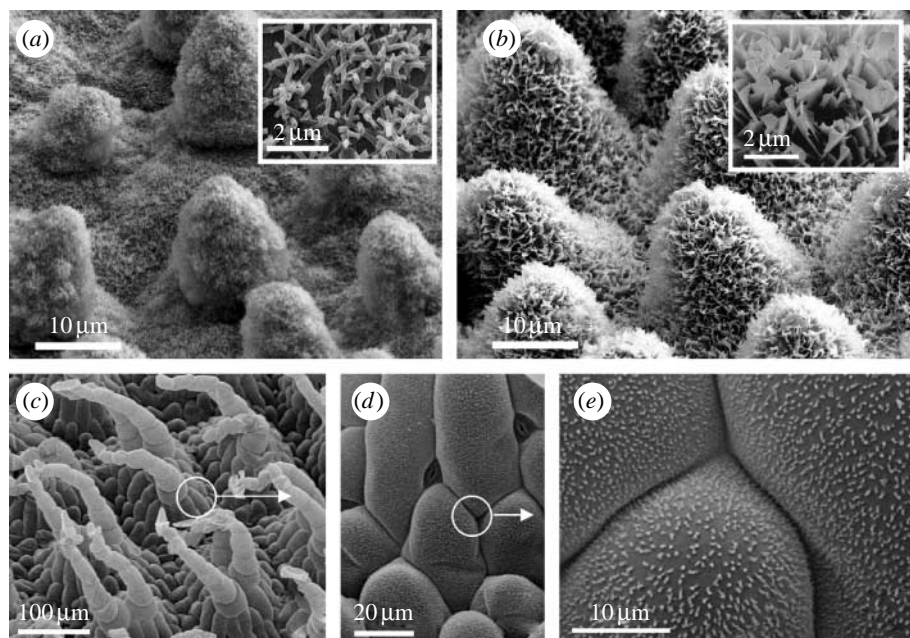
Figure 7. SEM micrographs of two kinds of hierarchical structures in plants. (*a*) The lotus and (*b*) *Euphorbia myrsinites* leaves are representative examples for the hierarchical structures composed of convex (papillose) cells with superimposed nanostructure forming wax crystals. The waxes shown in the inserts are tubules (lotus) and platelets (*Euphorbia*). (*c–e*) The SEM micrographs show the hierarchical structure of *Salvinia oblongifolia* hairs, composed of the multicellular hair with small rodlet-like wax crystals on top.

structuring. The first two levels are formed by the convex cells with superimposed three-dimensional wax crystals, and a third level of surface structuring is caused by the large hairs itself.

(*b*) *Biological significance of superhydrophobicity and self-cleaning*

The self-cleaning of plant surfaces by water repellence is a smart protection against particle accumulation. Superhydrophobic surfaces have been frequently found in wetland plants (Neinhius & Barthlott 1997). In these humid environments, the growth of most micro-organisms is provided by permanent or temporary water availability, and, under suitable conditions, micro-organism proliferation results in the formation of larger populations of micro-organisms, called biofilms. Thus, superhydrophobicity is also a protection against plant pathogens such as fungi and bacteria, because germination of many micro-organisms such as fungi and reproduction of bacteria are limited by water access (Stosch *et al.* 2007).

Superhydrophobicity prevents the formation of water films on the surface, which reduces the gas exchange dramatically. On wet leaves, where a liquid water film exists, the uptake of CO_2 for photosynthesis is reduced, because CO_2 diffuses 10 000 times more slowly through water than air (Brewer *et al.* 1991). Air layers or 'gas films' on submerged leaves enable a continued gas exchange via stomata and thus bypassing of cuticle resistance, enhancing the exchange of

O_2 and CO_2 with the surrounding water, and therefore underwater photosynthesis and respiration (Colmer & Pederson 2008). Raven (2008) discussed the phenomena of air-retaining surfaces in water and wetland plants and concluded that the occurrence of air films on submerged leaves could contribute to survival, if not growth, of wetland plants during temporary submergence.

Thus, we can conclude that superhydrophobicity in terrestrial plant surfaces can provide pathogen defence by self-cleaning or by the reduction of water availability for the micro-organism. Therefore, superhydrophobicity prevents biofilm formation and a reduction of gas exchange with the environment caused by the formation of water films.

3. Superhydrophilic plant surfaces

Superhydrophilicity has been developed by different organs of plants, in different phylogenetic independent groups of plants, and is caused by different micro- and nanostructures. The structural basics for superhydrophilicity in plants is shown in figure 8. Superhydrophilic plant surfaces can be divided into those that are permanently wet, absorb water over their surfaces and let water spread over the surface.

Permanent wet surfaces occur in submerged growing water plants. Extensive SEM analysis of water plants showed that submerged leaves have relatively smooth cell surfaces (tabular or slightly convex cells) and no three-dimensional waxes, cell papilla or hairs (Neinhuis & Barthlott 1997). In figure 8*a*, a characteristic surface structure of submerged growing water plants (*Anubias barteri*) is shown.

Water-absorbing structures in plant surfaces are pores, porous surfaces and multicellular hairs. Peat moss (*Sphagnum*), shown in figure 8*b*, has a sponge-like surface structure, formed by pores of 10–20 μm in diameter within the epidermis. Water uptake of up to 20 times of their own dry weight occurs via these pores (Ennos & Sheffield 2000). The pores in *Sphagnum* species arise by the rupture of the outermost membrane of single so-called hyaline cells (Mozingo *et al.* 1969). In figure 8*c*, the porous surface structure of the leaf of the moss *Rhacocarpus purpurescens* is shown. Here, the openings for water uptake are between 0.2 and 1 μm, much smaller than the above-described pores. The porous surface texture can be found within a single cell surface. The pores create a reticulate surface pattern and origin by the perforation of the outermost layer of the cell. The function of the porous surface structure is a rapid absorption of fog, dew or rain (Edelmann *et al.* 1998). Some desert plants are also able to absorb water via their surfaces. In the cactus family, leaves are reduced to spines (botanically thorns), and some species, such as *Turbinicarpus klinkerianus* and *Discocactus horstii*, are able to absorb water over the porous surface of their thorns (Schill & Barthlott 1973). Aerial roots of epiphytic orchids have a water-absorbing, porous outermost layer called velamen radicum. The velamen radicum is a special epidermis occurring only in aerial roots. The sponge-like structure of these roots consists mostly of dead cells (Capesius & Barthlott 1975).

Another superhydrophilic structure for water uptake via the surface is formed by absorptive hairs (hydathodes). All specimens within the *Bromelia* family, e.g. pineapple (*Ananas comosus*) or Spanish moss (*Tillandsia usneoides*), developed water-absorbing, multicellular absorptive trichomes, as shown in figure 8*d*.
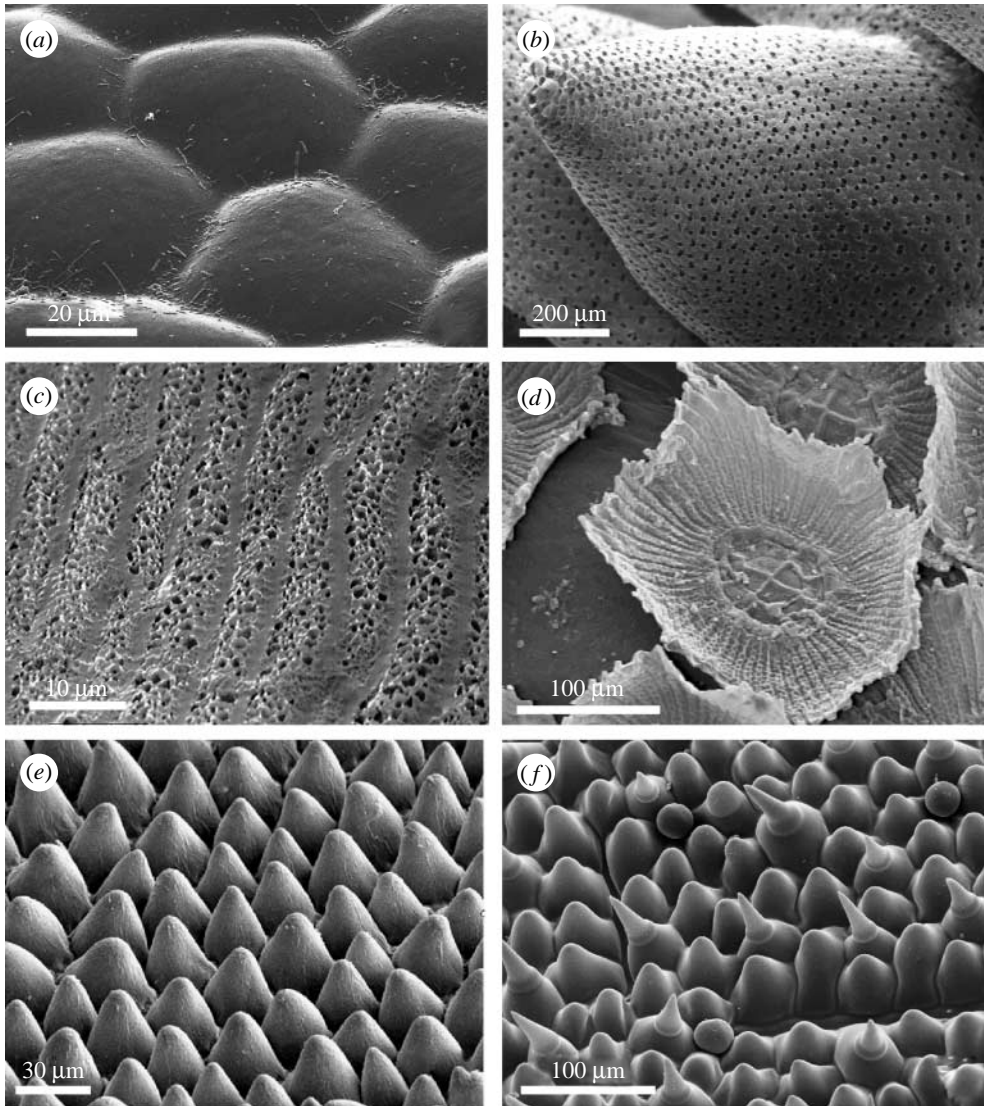
Figure 8. SEM micrographs of superhydrophilic plant surfaces. (*a*) The flat and unstructured surface of the water plant (*Anubias barteri*) is shown. (*b*) The surface of a water-adsorbing moss (*Sphagnum squarrosum*) is shown. In this, the pores are formed by dead and collapsed cells. (*c*) The water-adsorbing porous cell structure of the epidermis of moss *Rhacocarpus purpurescens* is shown. (*d*) The epiphytic growing Spanish moss (*Tillandsia usneoides*) with its characteristic multicellular water-absorbing hairs is shown. (*e*) The uniform conical cells on a leaf of *Calathea zebrina* and (*f*) the composition of different cell types of the superhydrophilic leaves of *Ruellia devosiana* are shown.

On some superhydrophilic plant surfaces, water spreads rapidly to a flat film. The carnivorous pitcher plants within the genus *Nepenthes* form pitfall traps to capture and digest arthropod prey. In many species, e.g. *N. rafflesiana*, insects become trapped by 'aquaplaning' on the wet pitcher rim (peristome; Bohn & Federle 2004). The microstructure of the peristome shows ridges, which mostly

extend into tooth-like structures at the inner edge and where the nectaries (nectar-secreting glands) are situated. Water droplets spread rapidly on the peristome and form thin films, which make the peristome extremely slippery for insects (Bauer et al. 2008).

The leaves of *Maranta leuconeura* and *Calathea zebrina* show a relatively homogeneous structure of conical epidermal cells (figure 8e). A droplet of water spreads on these leaves and a CA of 0° is reached within a few seconds. However, the fastest spreading of water observed in plant surfaces has been found in the leaves of *Ruellia devosiana* (Koch et al. in press). An applied 5 μl droplet of water needs 0.2 s for total spreading (static CA = 0°) on the leaf surface. A photo of the superhydrophilic moistened leaf is shown in figure 5. SEM and light microscopy have been used to characterize the leaf surface structures. The SEM image in figure 8f shows that the leaf surface is composed of different cell types: hair papilla; papilla cells; glands; and some extended, channel-like structures. The latter ones are formed by large elongated, flat cells that are surrounded by papilla cells. The glands secrete hydrophilic substances that, in combination with the surface roughness, lead to superhydrophilicity. Water on these leaves can also flow against the force of gravity. Such water flow is induced by capillary suction and has been quantified by measuring the water flow on horizontally and vertically oriented leaf stripes (5 cm length and 0.5 cm width). In horizontally orientated leaf stripes, the forefront of the moving water needed 11 s for a distance of 5 cm. In the vertically oriented specimen, the flow occurred against the force of gravity, and the forefront of the water needed 31 s to move 5 cm. Further data, including a description of the complex surface architecture, dimensions and frequency of structures of the leaves are presented in Koch et al. (in press).

(a) Biological advantage of superhydrophilic surfaces

An obvious advantage of permanent wetting in submerged growing water plants is that the plants have no drought-induced stress. However, water on the surface decreases the gas exchanges over the plant surface and can also lead to the formation of biofilms. Both consequences can reduce the activity of plant photosynthesis.

In other cases, superhydrophilicity is the basis for water and nutrient uptake for many lower plants, such as liverworts, lichens and some mosses, that have no roots for water uptake and no vascular system for water transport. In these species, the uptake of water and nutrients occurs over their complete surfaces. However, in some higher plants, e.g. the *Bromeliaceae* and epiphytic growing orchids, superhydrophilic surfaces have also been evolved for water and nutrient uptake.

The superhydrophilicity in carnivorous plants is used for insect capturing and therefore also functions for plant nutrition. The function of water spreading on leaf surfaces that do not absorb nutrients is less obvious. The spreading of water, e.g. on the leaves of *Ruellia devosiana*, provides a faster evaporation of the water by an increase of the water–air interface. Thus, water evaporates from a superhydrophilic leaf much faster than that from a hydrophilic or super-hydrophobic one, where water forms semi-spherical or spherical droplets. In habitats with frequent rain, such as tropical rainforests, this might be a

successful strategy to reduce the growth of micro-organisms and increase the gas exchange with the environment. In *Ruellia devosiana*, the combination of structural roughness and secretion of hydrophilic components allow the water and molecules within the water to spread over the whole leaf surface. The surface active components have not yet been determined, but two observations, and the fact that *Ruellia* belongs to the Acanthaceae, a family in which saponins are frequently found, lead to the assumption that these components are saponins. One observation was that the washing of the leaves in water leads to foam formation, as known for saponins. Another very interesting observation was made during the SEM investigations of the leaves. Even mature leaves, grown for several months in a tropical climate in a green house, showed no indication of any biofilm formation on the leaves. Saponins have detergent properties, which reduce the surface tension of the water and are known for their antimicrobial and antifungal properties (Osborne 1996). Based on these observations, we assume that saponins cause the efficient spreading of water, and spreading of the water–saponin solution functions as an efficient mechanism of self-protection against biofilm formation. However, further chemical analysis will prove this theory.

4. Wettability of plant surfaces as an inspiration for biomimetics

(*a*) *Superhydrophobicity for self-cleaning*

Self-cleaning surfaces require a certain degree of surface roughness in the micro- and nanoscale dimensions; thus, for the maintenance of material functionality, the materials must either be very wear resistant or the uses must involve low friction (Nosonovsky & Bhushan 2008*a*). For self-cleaning, moving of water is required, and applications where surfaces are exposed to rain or where surfaces can be artificially sprayed or rinsed with water are preferred. For self-cleaning by moving water, the surface must be superhydrophobic and the CAH should be less than 10°. Additionally, the aspect ratio and density of microstructures must allow the penetration of the water droplets between the pillars to collect small particles from the surface. Inspired by the self-cleaning behaviour of lotus leaves, various artificial superhydrophobic self-cleaning surfaces have been fabricated by creating appropriate surface morphology and roughness (Roach *et al.* 2008). A number of artificial roughness-induced superhydrophobic surfaces with hierarchical structures have been fabricated using electrodeposition, nano-lithography, colloidal systems and photolithography (Madou 2002; Ming *et al.* 2005; Chow 2007; Bhushan 2008). Patankar (2004) used the lotus leaves as a model to calculate the wetting of double-structured surfaces and showed that hierarchical structures (double roughness structures) are appropriate surface geometries that can be used to develop artificial self-cleaning surfaces. Based on Patankar's calculations, Martines *et al.* (2005) developed such microstructured silicon surfaces and confirmed that a pattern of slender pillars leads to the most stable water-repellent texture. Their findings also support the suggestion that the epicuticular wax crystals of the lotus leaf play the main role in its water-repellent behaviour. Based on a precise and low-cost replica technique (Koch *et al.* 2008*b*), superhydrophobic surfaces mimicking the hierarchical structures of plant leaves have been developed and optimized surface parameters for high

static CA and low CAH were identified (Bhushan *et al.* 2008, 2009). In these studies, hierarchical structures have been developed by a replication of a microstructured silicon surface. The second level of the hierarchical structure has been developed by thermal evaporation and subsequent self-assembly of hydrophobic plant waxes (tubules) and single aliphatic wax compounds (hexatriacontane), which mimic wax platelets known from plant surfaces. On smooth surfaces, wax tubules create superhydrophobicity (Niemietz *et al.* submitted), but superhydrophobicity combined with a low CAH was found only in hierarchical structures (Bhushan *et al.* 2008, 2009).

A patent on technical micro- and nanostructured self-cleaning surfaces was assigned to Barthlott (1998). Based on this, the trademark lotus effect has been introduced, and several industrial manufacturers developed products. The first product available was a façade paint that has been on the market since 1999. Further products are sprays for temporary superhydrophobicity on artificial surfaces. Such layers can, if no longer required, simply be removed by wiping. Self-cleaning glass lenses have been installed in sensors of traffic control units on German autobahns, and the introduction of building textiles, including awnings, tents and flags is to be expected. The list of the existing products for external surfaces includes lacquers for vehicles, waterproofed clothes and other textiles, and temporary coatings and plastics, e.g. microfluidic systems. The most important technique for the development of superhydrophobic, self-cleaning surfaces for glassware, buildings, vehicles, lighting and optical sensing is coating. Coatings can be formed as matte, semi-matte and most importantly also as a fully transparent and permanent coating. The coatings contain functional pigments, nanoparticles, binders and transport media and the surface structures are on the scale of several nanometres up to $50\,\mu m$ (Baumann *et al.* 2003). Polyester textiles, conventional polyester and microfibre polyester fabrics can be hydrophobized by using a water-repellent silicone coating procedure (Gao & McCarthy 2006). The temporary spray coating is a concentrated dispersion of superhydrophobic nanoparticles designed to equip a multitude of surfaces (Müller & Winter 2004).

(*b*) *Superhydrophobicity for underwater use*

For technical surfaces, the advantage of staying dry under water is the reduction of drag during movement. A small layer of air on a superhydrophobic surface reduces friction drag by 80 per cent at a speed of $4\,\mathrm{ms}^{-1}$, and 55 per cent at $8\,\mathrm{ms}^{-1}$ (Tokunaga *et al.* 1993; Fukuda *et al.* 2000). Marmur (2006) characterized superhydrophobic surfaces for underwater use and concluded that solid surfaces of a high roughness ratio might be optimal to keep the water surface as close as possible to the top of the roughness asperities. Such superhydrophobic, high-aspect ratio surfaces have been developed several times in nature and provided a guide for the development of air-retaining materials.

The surfaces of a number of floating plants and semiaquatic animals provide technical solutions for the design of underwater air-trapping surfaces, and some have recently been successfully transferred to technical prototypes (Solga *et al.* 2007; Cerman *et al.* 2009). Solga *et al.* (2007) and Cerman *et al.* (2009) studied the morphology and capacity for air retention of the surfaces of several species of the floating water fern *Salvinia* and some semiaquatic animals, such as water

spiders. The leaves of the water fern *Salvinia* are able to retain air films under water for up to 17 days. Based on these biological air-retaining surfaces, five surface characteristics for a stable long-lasting underwater air film have been identified. These include hydrophobicity; hairs with lengths of a few micrometres to several millimetres; additional fine structures such as ridges, hairs or waxes; micro- and nanocavities; and elasticity of the structures. Based on these characteristics, a prototype that stays dry for approximately 4 days when submerged in water has been developed (figure 9) by Cerman *et al.* (2009). For production, they used a silicon-based dental casting compound to generate replicas of *Salvinia* surfaces and filled the flexible and rubber-like silicon negatives of the plant surfaces with conventional acrylic varnish. Subsequent coating with a fluorocarbon hydrophobing agent (Antispread F 2/50 FK 60) made the surface water repellent. A patent for air-retaining surfaces has been submitted outlining different fields of application, such as textiles, varnishes and coatings by Cerman *et al.* (2006). In future, superhydrophobic air-retaining surfaces, which reduce drag during movement in water, might be a smart solution for energy-saving surfaces, such as the walls of pipes or boats (Nosonovsky & Bhushan 2008*b*).

Underwater superhydrophobicity might also be a solution for the reduction of the accumulation of sessile marine organisms such as algae, bacteria, and others on underwater surfaces. Genzer & Efimenko (2006) present implications of superhydrophobicity on marine fouling and potential designs of coatings and roughness on multiple length scales, as a promising platform for efficient foul-release marine coatings.

(*c*) *Existing and potential uses of superhydrophilic surfaces*

Superhydrophilic surfaces cause water to spread out. In plants, spreading of water can be induced not only by water-absorbing porous surface structures and hairs, but also by the structuring of hydrophilic surfaces. For a hydrophilic solid substrate, the liquid–solid contact is commonly governed by the Wenzel mode, and the hydrophilicity will be enhanced by the surface roughness and water spreads when the free surface energy is high. Such surfaces will naturally dry out quickly and prevent fogging up when in contact with steam or condensation. These properties are of special interest for several outdoor and indoor applications, such as windows, mirrors or shower screens. Additional applications include easy-clean household goods and road signs, anti-condensation air conditioners and anti-fouling paints (Gould 2003).

Another area where superhydrophilicity is essential is photocatalytic self-cleaning surfaces (Parkin & Palgrave 2005). In these surfaces, self-cleaning is based on a photocatalytic process, which causes a chemical breakdown of organic dirt adsorbed onto the hydrophilic surface when exposed to light (Fujishima *et al.* 1999). In simple words, the photocatalysis led to a conversion of organic molecules to carbon dioxide and water (and other products if heteroatoms are present). Such surfaces are covered with a thin transparent layer of titanium dioxide (titania or TiO_2). On the market are roof tiles, glasses for windows, outdoor tiles, paints and textiles impregnated with titania (Parkin & Palgrave 2005). Another field of potential use are nano- and microfluidic systems, with pressure-free transport of liquids.
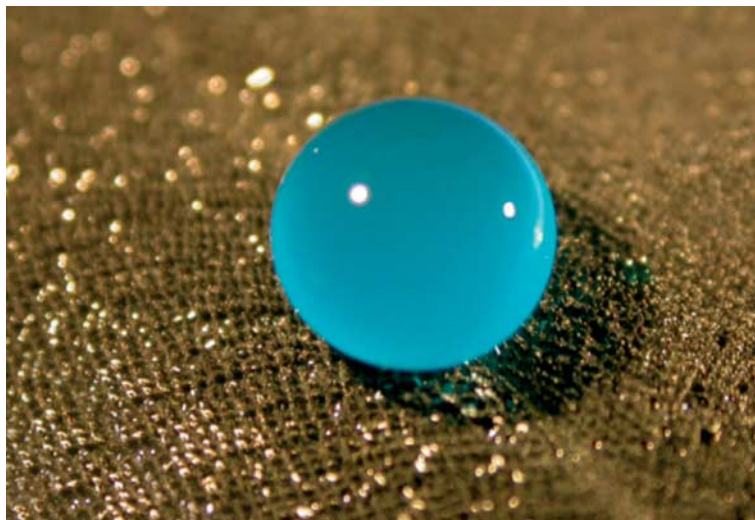
Figure 9. A biomimetic superhydrophobic surface of *Salvinia oblongifolia* leaf. The water droplet (stained with food dye) forms a nearly perfect sphere on the replica of the *Salvinia* leaf. The replica retains an air film when submerged under water for 4 days (adapted from Cerman *et al.* 2009). SEM figures of the leaf structure are shown in figure 7.

5. Conclusions

Plant surfaces provide the largest biological interface on Earth. Within millions of years of evolution, plants developed a large diversity of surfaces adapted to their specific environment. The structural basics of superhydrophobic plant surfaces are hierarchical structuring over two length scales, e.g. in lotus leaves, and three length scales in the water fern *Salvinia* have been introduced. The existing and potential uses of superhydrophobicity include a reduction of biofilm formation and self-cleaning. Drag reduction during movement in water by superhydrophobic air-retaining surfaces might also be a smart solution for the development of energy-saving surfaces of pipes or boats. Superhydrophilicity in plants not only is based on smooth surfaces in underwater growing plants, but is also caused by surface structuring, such as by water-absorbing hairs, porous and sponge-like structures and rough convex surface structures. The biological advantages of these wetting phenomena include water and nutrient absorption and a fast evaporation of water from the surfaces. Superhydrophilicity is advantageous to prevent droplet formation by condensation on surfaces and provides a smart strategy to prevent fogging of glasses, windows, mirrors and other surfaces. In future, the use of capillary water transport by superhydrophobic surfaces might be used for low-energy transport of liquids in micro- and capillary systems.

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