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DESIGN OF HIERARCHICALLY SCULPTURED BIOLOGICAL SURFACES WITH ANTI-ADHESIVE PROPERTIES

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ABSTRACT

In many plant species sophisticated functions such as water repellence, reduction of particle adhesion and reduction of insect attachment are correlated to a hierarchically sculptured surface design. One prominent example is given by the hierarchically sculptured, self-cleaning surface of the lotus leave (*Nelumbo nucifera*). In plants hierarchy of surfaces is often realized by combining microstructures with superimposed self-assembled nanostructures. Such functional biological surfaces are of great interest for the development of biomimetic self-cleaning materials. Examples of superhydrophobic plant surfaces are introduced here, and their hierarchical surface sculptures and existing and potential use of their properties in artificial materials are shown.

INTRODUCTION

The term *biomimetic* describes the study and transfer of nature's methods, mechanisms and processes into artificial materials and systems [1]. Biomimetic research deals with functional micro- and nanostructures and the transmission of biological principles such as self-organization and functional structures. To use nature's models in engineering one can take biological characteristics and develop analogue solvents for engineering. Several aspects, such as their energy harvesting system, their ability of self-healing and their multifunctional surface properties make plants interesting models in biomimetic research.

Approximately 460 million years ago, the first plants moved from their aqueous environment to the drier atmosphere on land. Since then, evolutionary processes led to physiological, chemical and morphological variations which enabled them to settle into nearly all conceivable habitats. The plant surface is in direct contact with the environment and therefore an important interface with different environmental influences. Adapted to their specific environmental approaches, *e.g.* efficient light reflection in desert plants, a large diversity of functional plant surface structures has evolved [2].

The epidermis is the outermost cell layer of the primary tissues of all leaves and several other organs of plants. The protective outer coverage of the epidermis is a continuous extracellular membrane, called the cuticle. The cuticle is basically composed by a polymer called cutin and integrated and superimposed lipids called “waxes” [3]. Only a few books summarize the intensive research and include further aspects, such as the biosynthesis of the plant cuticle [4, 5]. One of the most important properties of the cuticle is the transpiration barrier function, *e.g.* for the reduction of water loss and prevention of leaching of ions from the inside of the cells to the environment. The plant cuticle also plays an important role for insect and microorganism interaction. Their surface sculptures have a strong influence on the reflection of radiation, the surface wetting ability and adhesion of insects and contaminations [2]. Additionally, it is a mechanical stabilization element for the plant tissue [6].

Waxes are the hydrophobic component of the plant cuticle and are integrated (intracuticular) and superimposed (epicuticular) to the cuticle [3]. The epicuticular waxes form thin two-dimensional films and three-dimensional structures which cover the cuticle surface. Wax films are often combined with three-dimensional waxes, which occur in different morphologies like tubules, rodlets or platelets (Fig. 1) [7]. Both the films and the three-dimensional waxes have a crystalline structure [8]. Three-dimensional epicuticular wax structures occur in sizes from 0.5 to 100 µm, whereas two-dimensional wax films range from a few molecular layers up to 0.5 µm [7, 9]. The wax morphology originates by self-assembly [10] and is strongly correlated to the wax chemical composition [3, 11]. The chemistry of waxes is a mixture of long-chain hydrocarbons and, in some waxes, cyclic hydrocarbons. Substitution by functional groups (-hydroxyl, -carboxyl, -ketoyl) broadens the spectrum of compounds to fatty acids, aldehydes, *ß*-diketones and primary and secondary alcohols [3, 12]. The chemical composition of plant waxes is highly variable amongst plant species, the organs of one species, and varies during organ ontogeny [13].

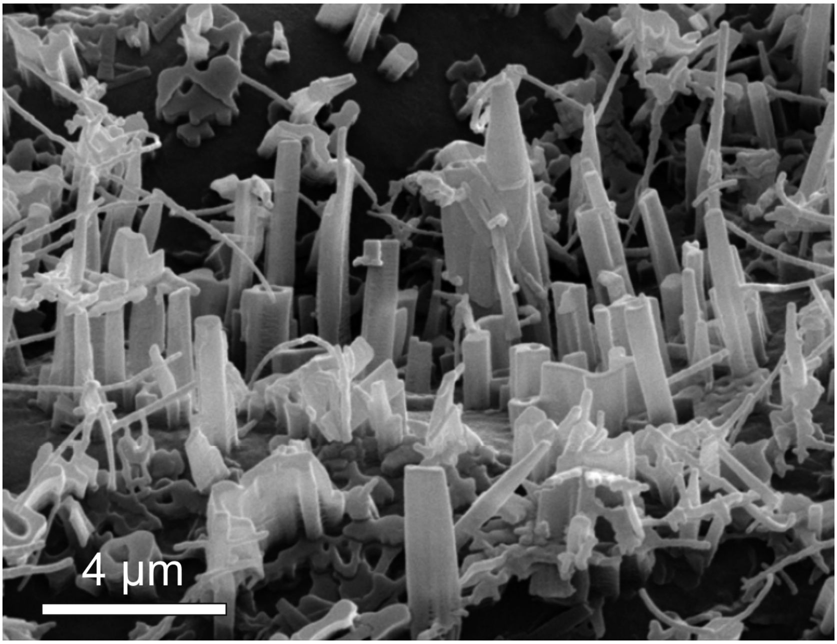

Figure 1. Scanning electron microscopy graph of epicuticular waxes on a cabbage leaf (*Brassica oleracea*) shows perpendicular orientated rodleds and interspersed some smaller wax filaments.

HIERARCHY IN PLANT SURFACES

Hierarchy of the plant surface sculptures is based on the combination of sculptural elements of different scale sizes. In the following examples the defined level of hierarchy start at the macro-scale and are subdivided into further hierarchical levels with smaller sculptural elements. The sculptural subunits in the macro-dimension range in the sizes of some millimetres, *e.g.* the waviness of a leaf plane. Multi-cellular sculptures, such as the hairs shown in Figure 3, can create a second level of sculptural elements. Within the next smaller level, which covers sculptures of several microns, the outline of surface cells creates a sculpturing. The outline of single cells can be convex (arced to the outside) or concave (arced to the inside). The convex cell type is the most common one and is often found on flower-leaves, stems and leaves [14]. A description of different cell morphologies and cell outlines is given by Barthlott and Ehler [15] and Koch *et al.* [2]. Within the next smaller level, which covers sculptures of up to a few micrometer down to sub-micrometer scale sizes, sculptures, such as cuticular folds and the wax crystals are relevant.

HIERARCHICAL SURFACE SCULPTURES FOR SUPERHYDROPHOBICITY AND SELF-CLEANING

Hierarchical sculptures play a key role in surface wetting [16] and are discussed in this paper in the context of superhydrophobicity. Superhydrophobic surfaces play an important role in technical applications ranging from self-cleaning window glasses, paints, and textiles [17] and include low-friction surfaces for fluid flow [18] and energy conservation [19]. Such superhydrophobic surfaces are characterized by a high static contact angle (> 150°), and in the case of self-cleaning surfaces also show a low contact angle hysteresis (the difference between the advancing and receding contact angles) of less than 10° and a low tilting angle (< 10°).

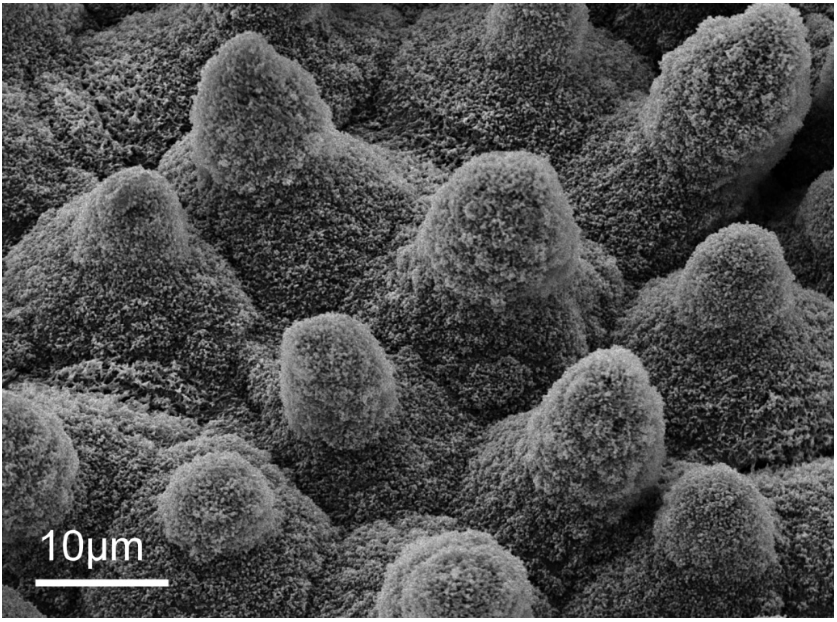

Figure 2. Scanning electron micrograph of the lotus leaf surfaces shows the papilla shaped cells, covered a nanostructure of wax tubules.

The most prominent self-cleaning surfaces in nature are the lotus leaves (*Nelumbo nucifera*). On lotus leaves, water droplets roll over the leaf surface and collect dirt and other particles from the surfaces. Lotus leaves have been the inspiration for the development of several artificial self-cleaning biomimetic materials [17, 20]. The superhydrophobicity and self-cleaning of the lotus leaves (Fig. 2) were found to be a result of a hierarchical surface structure, built by randomly oriented small hydrophobic wax tubules on the top of convex cell papillae [21, 22]. The wax tubules on lotus leaves, shown in Figure 2, are usually 0.3 to 1.1 μm in length and 0.1 to 0.2 μm in diameter [11]. In most plant species, superhydrophobic surfaces are designed by a two-level surface sculpturing: convex (papillose) sculptured cells covered with three-dimensional waxes [23]. In different studies, artificial superhydrophobic surfaces with surface sculpturing only on the nano-scale level have been fabricated [24], but hierarchy in surface sculpturing has been shown to further reduce the adhesion (hysteresis) of liquids and water droplets roll off at very low tilt angles, a condition required for self-cleaning [20, 21, 23, 25, 26 – 28]. A plausible explanation for these phenomena can be found in Wentzel's explanations [29]. Wentzel suggested a simple model predicting that the wetting ability of a liquid, measured as the contact angle, with a rough surface is different from that with a smooth surface and that a hydrophobic surface gets more hydrophobic with the increase of the surface roughness. Later, Cassie and Baxter [30] showed that a gaseous phase, commonly referred to as "air", may be trapped in the cavities of a rough surface, resulting in a composite solid-liquid-air interface. Nowadays, a large number of studies give evidence that water repellence and self-cleaning of superhydrophobic surfaces are caused by a reduction of both the contact area and the adhesion of contaminations and water to the surface [31, 32].

As mentioned above, the lotus leaf surface has been termed a two-level hierarchical surface. Recently, cryo-scanning electron microscopy showed that the minimized contact area of a lotus leaf and an applied liquid (a glycerol-water mixture) is caused by a four-level surface sculpturing [33]. At the scale of several hundreds of microns the waviness of the lotus leaf surface causes large air pockets, in which several cells are only in contact with the air captured under the water droplet. The second hierarchical level is given by the variations in epidermal cell heights. In those areas where the leaf surface is in contact with the liquid, only the higher cells are in contact with the liquid. The third level of hierarchy, which has an influence on the contact area, is provided by the clusters formed by the wax tubules. Such clusters are randomly interspersed within the surface and they are higher than the surrounding wax tubules. The fourth level of hierarchy which reduces the water-surface contact area is given by the single tubules emerging out of the wax clusters [34].

HIERARCHY IN SUPERHYDROPHOBIC SURFACES FOR UNDERWATER USE

Underwater air-retaining surfaces are of great technological, economic and ecological interest because the trapped air minimizes the water-solid contact area and leads to a reduction of frictional drag between surface and water [35, 36]. Floating plants of the genus *Salvinia* possess superhydrophobic leaf surfaces which are adapted to efficiently retain a layer of air when submerged under water [18]. Immersed in water the leaves are capable of holding an air layer for several weeks. The upper sides of the floating leaves of *Salvinia* are covered with multicellular hairs (Fig. 3). Water applied onto the leaf stays on top of the hairs without sinking in between the structures and the water is not able to penetrate between the hairs; thus forming an air-water interface between the tips of the hairs and the applied water. For long term air retention the stabilization of this air-water interface at a predefined level at the top of the hairs is crucial. Scanning electron microscopy studies of *Salvinia molesta* leaves showed that six levels of surface sculptures exist. The first level is given by the arrangement of several multicellular hairs (also known as “eggbeater” hairs) within the leaf plane. The individual hairs, variations in their sizes and their orientation provide the second level of surfaces sculpturing. The convex epidermis cells of the hairs are the third level of sculpturing.

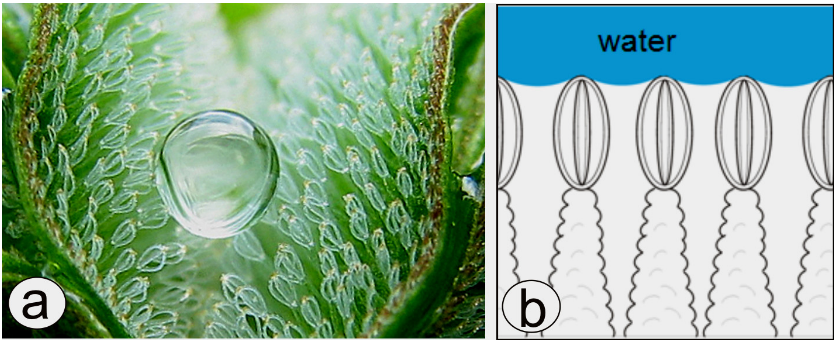

Figure 3. The water fern Salvinia as model for underwater air retaining surfaces. **(a)** shows a water droplet on the superhydrophobic leaf of the water fern *Salvinia molesta*. In **(b)** the schematic shows the eggbeater shaped hairs of *Salvinia* surrounded by air, when immersed under water.

The fourth level is given by the three-dimensional wax crystals, which appear in two different sizes and morphologies. The larger wax rodlets provide the fourth level, whereas the fifth level of sculpture is given by smaller wax filaments. The wax rodlets have a height of approximately 300 nm and the height of the small wax filaments between the rodlets is approximately 30 nm. Finally, the wax rodlets possess another level of surface sculpturing formed by small filament-like structures. The terminal cells of each hair lack the wax crystals and are in contrast to the rest of the upper leaf surface not superhydrophobic but hydrophilic. These hydrophilic patches pin the air-water interface to the tips of the hairs and thus decrease the risk of delamination of the water layer. For artificial air-retaining surfaces, Barthlott *et al.* [18] expect a wide range of applications, including drag-reducing ship coatings, low-friction fluid transport and novel concepts for thermally insulating interfaces.

SLIDING STRUCTURES FOR INSECT CAPTURE

The examples introduced here show that multilevel hierarchically surface sculpturing can provide water repellent, self-cleaning or underwater air-retaining surfaces with drag-reducing properties. Hierarchy in surface sculpturing can also play a key role in anti-adhesive surfaces. Poppinga *et al.* [37] investigated by scanning electron microscopy the surface sculptures of 53 different plants species with pitfall traps for capturing insects. Two groups of flowering plants specialized in insect catching were investigated. The carnivorous plants catch prey for a substantial nutrient supply [38] and plants with kettle traps, temporarily capture their pollinators [39]. With special adhesive devices, insects, *e.g.* flies are able to attach to rough or smooth surfaces. On rough surfaces, claws allow anchorage via hooking, whereas smooth adhesive pads or hairy pads enable adhesion via van-der-Waals and capillary forces on smooth surfaces [40 – 42]. Interestingly, these mechanisms fail on the plant traps and the insects lose their foothold. Such slippery plant surfaces might play an important role as templates for a transfer into technical materials for insect pest control. Poppinga *et al.* [37] revealed that in pitfall traps combinations of epidermal cell curvatures, cuticular folding, three-dimensional epicuticular wax crystals and idioblastic elements exist. The most prevalent cell shape, found in 35 species, is papillae cells with downwards leading orientation. 29 species showed two or three levels of surface sculptures. Examples of two-level sculptures are *Aristolochia pearcei* (Fig. 4a) with papillate epidermal cells covered with waxes and *Cephalotus follicularis* (Fig. 4b) with papillate epidermal cells and cuticular folds. Sliding structures with a three-level hierarchical sculpture were found in *e.g. Sarracenia leucophylla*, with papillate epidermal cells and cuticle folding with superimposed epicuticular waxes (Fig. 4c).

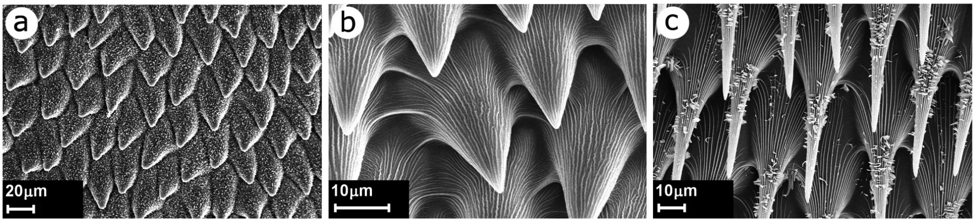

Figure 4. Scaning electron micrographes of slipery plant surfaces. In **(a)** *Aristolochia pearcei* the surface sculptures are formed by papillate epidermal cells covered with waxes. In **(b)** the surface sculptures of *Cephalotus follicularis* are formed with papillate epidermal cells and cuticular folds. In *Sarracenia leucophylla* **(c)** downward pointing, papillate epidermal cell shape care combined with two superimposed fine structures (epicuticular waxes and cuticular folds). Photos from [37].

CONCLUSIONS

In most plants superhydrophobic surfaces are formed by microstructured cells with three-dimensional superimposed waxes, or by multi-cellular hairs, which are also covered by three-dimensional waxes. Hierarchical roughness of plant surfaces leads to self-cleaning or underwater air-retaining surfaces, as shown for the lotus leaves and the water fern *Salvinia*. Anti-adhesive “sliding structures” of plants are further examples of highly functional biological interfaces.

The structures of plant surfaces and their remarkable functions introduced here demonstrate that nature provides solutions for the development of artificial functional materials. The surface structures presented here are only a small fraction of existing structures, but they might stimulate the research in biomimicry, and might help to transfer the ideas and concepts implemented in nature into technology.

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