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LASER-BASED BIOMIMETIC FUNCTIONALIZATION OF SURFACES: FROM MOISTURE HARVESTING LIZARDS TO SPECIFIC FLUID TRANSPORT SYSTEMS

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ABSTRACT

Inspirations found in nature became more and more famous for an innovative product development. An interdisciplinary approach of scientific research and industrial development has shown that identification and transfer of biological principles to technical applications uncover secrets of specific adaptations resulting in innovations with remarkable potential.

Investigating the functional morphology of moisture harvesting lizards revealed the underlying principles of an adaptation to a life in arid environments. To survive water scarcity these lizards have developed different water catchment strategies. Special skin structures enable them to acquire water from moist substrate and transport the collected water to the snout. The former is a micro ornamentation, which can hold a water film to render the surface superhydrophilic, the latter is a network of half-open capillary channels that transports the collected water. Transferring these structures to a producible structure design and to technical surfaces requires a fundamental understanding of the biological principles as well as an abstraction and modification. Additionally enabling manufacturing technologies like laser structuring are needed to realize a functional surface structuring on complex shaped products. It is concluded that a biomimetic liquid transport can increase the product performance, improves product life time or saves resources.

Keywords: capillary, laser surface structuring, moisture harvesting, passive fluid transport, surface functionalization, wetting.

1 INTRODUCTION

The main challenge for living species to survive in an arid or semi-arid environment is low availability of water. Living in such regions of water scarcity demands special evolutionary adaptations. The most important adaptation of lizards has evolved convergently in the Texas Horned lizard (Iguanidae: *Phrynosoma cornutum*) and the Australian Thorny devil (Agamidae: *Moloch horridus*). Both species are able to collect and transport water passively with their skin and without any movement or energy consumption. This name-giving ability of moisture harvesting commonly comprises an accompanying behaviour [1, 2, 3, 4] as well as a superwettable skin and water transport with capillary channels as two physical features.

The integument (Latin: integere = to cover; i.e. skin plus derivates like scales) provides a micro ornamentation on the scales [5], which can hold a water film causing the surface to become superwettable. This improved wettability (i.e. from hydrophilic to superhydrophilic skin properties with a contact angle below 10°) can be achieved by water coverage of 73% of the body's surface [6].

In capillary channels formed by partially overlapping (imbricate) scales, collected water is transported further to the snout where active water ingestion takes place [7, 8, 9, 10]. These channels have a narrow opening on their superficial side and thus form a semi-tubular capillary system over the entire lizard's body [7]. A transportation of water to the snout is necessary, because the integument is found to be almost waterproof to minimize evaporational water loss [11].

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Besides the biological relevance, the functional morphology of the lizards' integument might also be of technical interest wherever there is a demand of efficient collection of small amounts of liquids and/or a passive transport of these liquids. Such kind of inspirations found in nature became more and more famous for an innovative product development [12, 13, 14].

A biomimetic 'bottom-up' approach was used to analyse the biological model and to abstract and transfer natural structure characteristics to synthetic structure patterns for final usage on various fields of application. That transfer of lizard skin structures to technical applications is presented by fabrication of first demonstrators. For fabrication of deduced micro structures the micro manufacturing technology of laser surface structuring was used. Especially ultra-short pulse laser enable a high precision machining. Wetting tests performed on laser structured steel surfaces were conducted with oil as this is one of the most important material-liquid combinations in the field of mechanical engineering.

2 RESULTS AND DISCUSSION

2.1 Morphology

The skin morphology of different moisture harvesting lizards like the Texas horned lizard (*Phrynosoma cornutum*) and the Australian thorny devil (*Moloch horridus*) was investigated regarding a potential influence on wettability and water transport.

P. cornutum exhibits three major scale types, differing a lot between body regions (Fig. 1 A-F). The largest scale type are the spines, which are larger than surrounding scales and found dorsal (Fig. 1 A) and around the head (Fig. 1 E). A second scale type is more or less mucronate, hexagonal

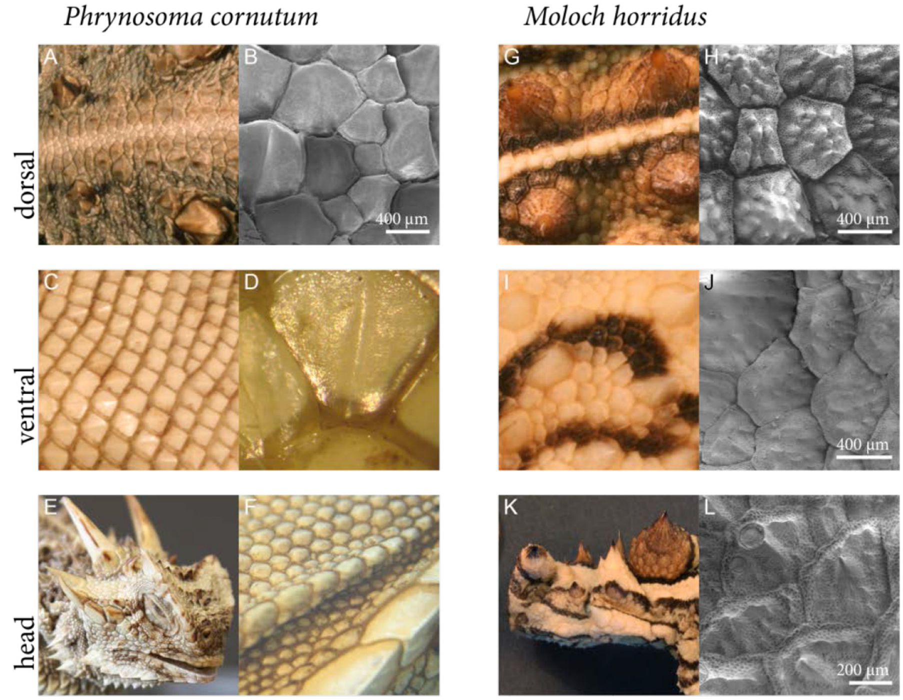

Figure 1: Scale types of moisture harvesting lizards (A-F) *Phrynosoma cornutum* (G-L) *Moloch horridus*.

to polygonal and either quite homogeneous in size (ventral) or heterogeneous (dorsal). The third type is almost circular, quite homogeneous in size and found at the lower part of the head. Despite the spines, an average scale size from about 0.02 mm² to more than 2.5 mm² is found.

Despite this more heterogeneous shape of scales, *M. horridus* shows only two major scale types, spines and pentagonal to hexagonal scales with an inconsistent number of small protuberances (Fig. 1 G-L). Independent of body regions spines are much larger than scales. Both types are distributed over the entire body surface, but smaller on ventral side (Fig. 1 I-J). In general, the size of normal scales ranges from about 0.07 mm² to 0.33 mm².

The previous mentioned micro ornamentation [5] differs between moisture harvesting species. *M. horridus* exhibits a strong pronounced micro ornamentation with an approximate depth of 5 μm, covering the entire scale surface. For *P. cornutum* a less pronounced micro ornamentation is found, with an increasing depth towards the edge of the scales (Fig. 2 B).

2.2 Switchable wettability

The common feature of the scales, independent of form or species, is their wettability. Applied water droplets immediately spread over the integument [6]. In contrast, applied droplets on the integument of non-moisture harvesting lizards like the so called sandfish (*Scincus scincus*) hardly spread [6].

Wetting behaviour of the skin of moisture harvesting lizards was first characterized by applying single water droplets onto different lizard species. These droplets spread immediately after application.

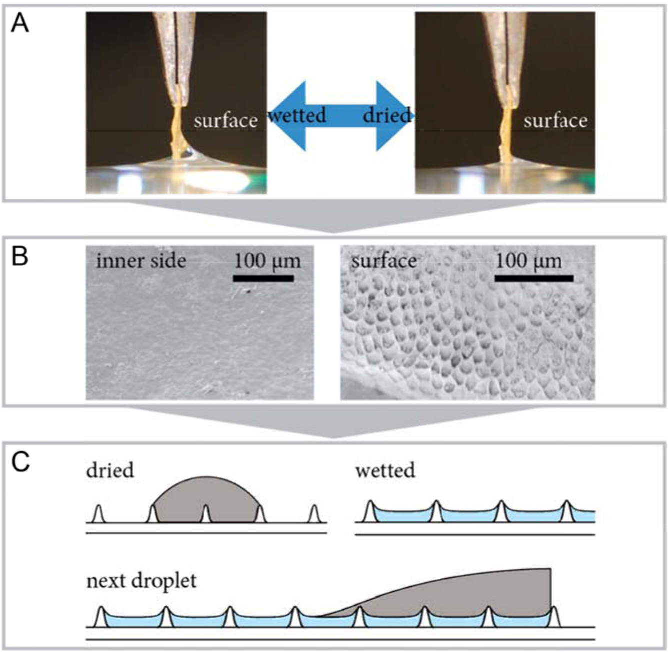

Figure 2: Wettability of a scale of *Phrynosoma cornutum*. A) In a wetted state a scale (sublabial region, Fig. 1 E) shows a remarkable different wettability between inner skin side and surface B) Both scale sides were analysed with SEM C) Schematic wetting model.

That spreading and a strong topography made standard contact angle measurements hardly possible. Therefore wettability was determined with a single dissected scale which was brought in contact with a water surface to illustrate the arising meniscus (Fig. 2 A). Several scales were tried, but a sublabial scale of *P. cornutum* worked best, due to its size and shape.

A freshly prepared scale exhibits a remarkable difference between the meniscuses at both sides (Fig. 2 A): While on the inner side a small meniscus (i.e. a large apparent contact angle) is formed, the scale surface is wetted with an apparent contact angle less than 10° (i.e. superhydrophilic). This superhydrophilicity diminishes if the experiment is repeated with a scale dried on silica. However, after immersing the scale in water, it again behaves like a freshly prepared scale. One can easily switch between these two states by drying or wetting the scale (Fig. 2 A).

As both sides consist of the same material (keratin), the only difference can be found in the structure. While the inner side of this particular scale is completely flat, the surface exhibits a distinct micro ornamentation, which appears to be a honeycomb like structure that is stronger pronounced towards the edge (bottom) of the scale (Fig. 2 B). The apparent contact angle on such structure, i.e. a composite material, can be described by Cassie-Baxter equation [15]:

$$\theta_{\text{Cassie}} = \gamma_1 \cos\theta_1 + \gamma_2 \cos\theta_2 \tag{1}$$

The apparent contact angle θ_{Cassie} is dependent on the area fraction γ and contact angle θ of component 1 (e.g. keratin) and area fraction γ and contact angle θ of component 2 (e.g. water).

The observed immediate spreading of water droplets on the skin of moisture harvesting lizards reveals superhydrophilic skin properties ($\theta_{Cassie} < 10°$). Based on the Cassie-Baxter equation Comanns *et al.* calculated that ≥ 73 % area fraction of water coverage is required to render the skin superhydrophilic [6]. Conversely, a keratin area fraction of 27% is needed.

As a further step, a model of pre-wetting can be derived from that calculation (Fig. 2). If the micro ornamentation is filled with water, the walls are the only free keratin surface. Assuming a hexagonal micro ornamentation with a wall width of 2 µm, a diameter of 17.1 µm would be a possible solution for a surface consisting of 27% keratin and 73% water. As the range of measured diameters is 10 µm to about 30 µm [6], the calculated diameter appears to prove the derived model of a switchable wetting.

The wetting principle of moisture harvesting lizards is a micro structure capable of holding a certain amount of liquid. The more liquid is structurally held the higher the wettability, because the contact angle is decreased. As there is a remarkable change in contact angle, the surface contains a switchable wetting behaviour as functionality. Here, switchability is achieved by the liquid itself, not by external stimuli like UV-light, temperature, pH change, current change, solvents or others [16].

2.3 Water transport

Applied water droplets on the lizards' skin do not spread over the entire skin surface, but only over a few scales. After some spreading, the applied water starts to flow in capillary channels between the scales (Fig. 3 A). Despite an irregular distribution of micro ornamentation [1, 9, 10], a subsequent capillary transport is a more likely reason for the observed phenomenon (Fig. 3).

Putting the observation into a model, structures for an adjustable wettability and a capillary water transport are assumed to complement each other to achieve the observed functionality. A micro ornamentation allows water droplets to wet the scale surface. A more distinctive micro ornamentation towards the edges of the scales (Fig. 2 C) potentially results in a gradually lower contact angle

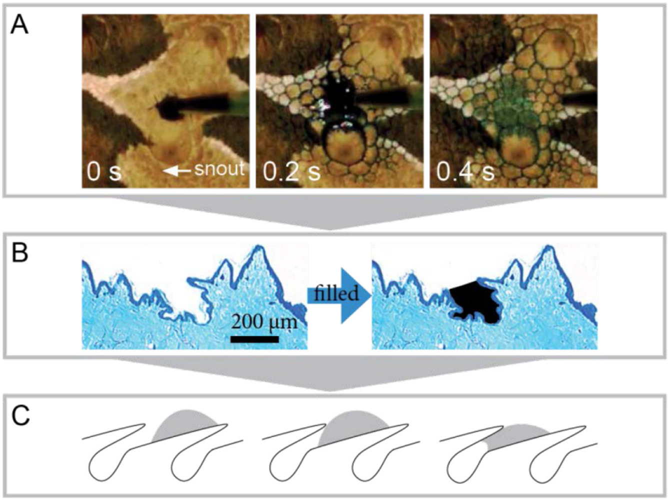

Figure 3: Water absorption of moisture harvesting lizards. A) Image sequence of applied water droplet (1% blue food colour) on dorsal side of *Moloch horridus* B) Histological slices of dorsal integument of *M. horridus* with cross section of half-open capillary channel (black area) C) Influence of surface wettability and capillary structure on water droplet.

in a wetted state. As a result the velocity of spreading droplets should increase towards the edge of scales. Reaching the imbricate overlapping scales spreading water droplets are soaked into the capillary structure between the scales where the water is transported further (Fig. 3 C).

2.4 Abstraction

A technical realisation and manufacturing of biological inspired, functionalised surfaces requires that surface functionalization matches with the functional principles of natural structures. The main demands are simplicity, scaling and material. Each demand requires an adjustment with regard to the application or product, and a sufficient abstraction.

The natural structures of lizards skin, i.e. micro ornamentation and capillary channels, have a great variation in size and shape. Especially an undercut structure is hardly producible. Therefore the complex natural structure was abstracted in a first approach to a quadrate cross sectional shape, where the widest part is at the surface (Fig. 4). Furthermore, significant structure features like radii, distances, depths etc. were defined for a suitable geometrical description (Fig. 4). This enables an easier identification of correlations between single, relevant features in future studies to gain a parameterized description.

For an adjustable wetting, micro structures with diameters in a range of 10 µm to 30 µm and a depth of 1 µm to 5 µm were identified. The capillary channels have dimensions of 50 µm to 300 µm in width and 30 µm to 70 µm in height. Thus structures, have different dimensions with benefits and disadvantages regarding the observed surface functionalities of adjustable wetting and water transport. It is possible to scale structure sizes up or down adapted to product dimensions complying the basic structure functionality (Fig. 5 A and B).

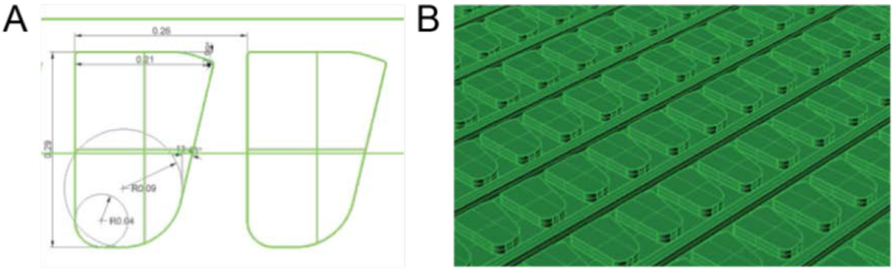

Figure 4: Construction of abstracted scale pattern for fabrication. A) Defining the geometrical parameters. B) 3D-model of the pattern.

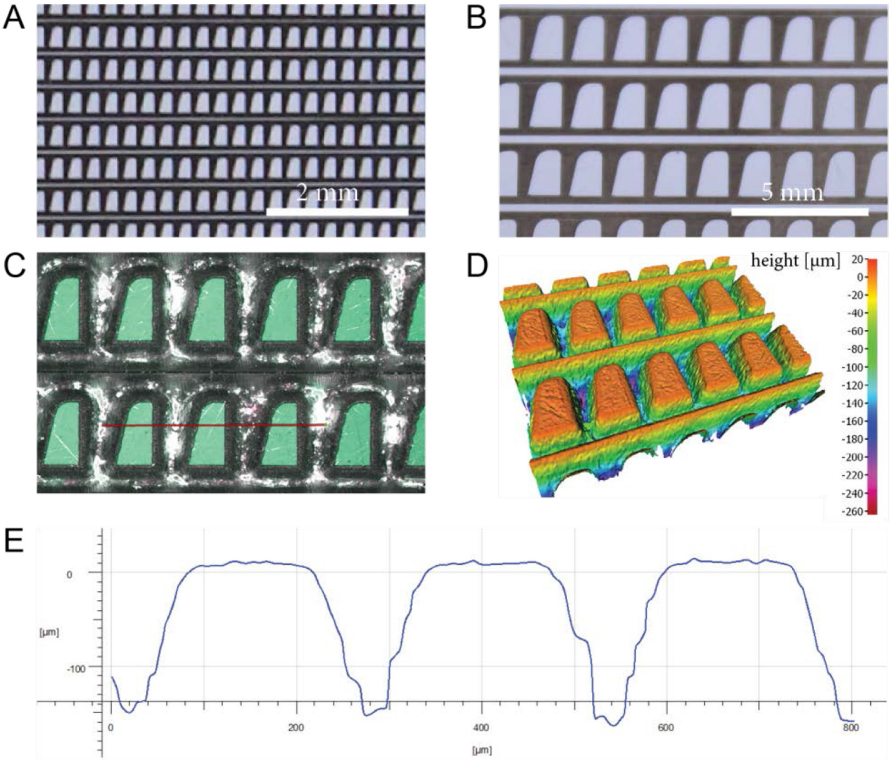

Figure 5: Fabrication of scale pattern in different scaling (1:1 and 6:1) and with analysis of topography. A) Technical structure in same dimension as natural. B) Technical structure 6 times larger than the natural structure. C) Top view with indicated analysis position (red line). D) 3D-image in false colour, indicating the depth. E) Structure height in cross sectional view along red line in C.

Besides the influence of structure characteristics on a surface-liquid interaction, wetting and water transport depend on material properties. As the contact angles of keratin and e.g. metal differ much, the material in a final application has a strong impact on functionality. Thus standardizations, and suitable material-liquid combinations are possible strategies to meet requirements regarding the

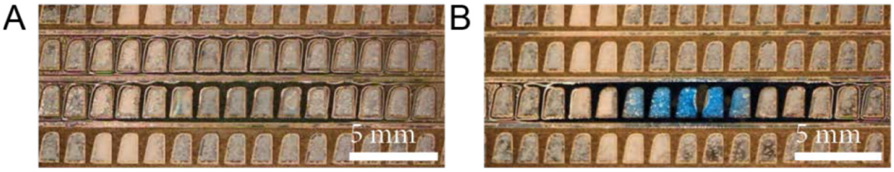

Figure 6: Functionality of manufactured scale patterns A) Coloured ethanol B) Coloured cutting oil, both on hot working tool steel 38CrMoV5-1 with a hardness of 52 HRC.

material properties. Ethanol or cutting oil, for example, can be transported in structure patterns on hot working tool steel (Fig. 6).

2.5 Laser structuring as an enabling manufacturing technology

The transfer of the observed skin functionality of moisture harvesting lizards to functionalised, technical surfaces requires a structure design suitable for fabrication.

Based on the parameterized information of abstracted structure patterns as seen in Fig. 4, engineers are able to model artificial structures with conventional CAD-programmes. Now, considering the structure dimensions and geometry, a suitable micro manufacturing technology has to be selected for an industrial realisation of a bionic functionalised surface. Electro discharging machining and micro milling are established manufacturing technologies in the industrial field of micro machining, e.g. in the watch manufacturing industry or in the medical sector [17]. However, laser surface structuring as an innovative manufacturing technology has become more and more important in the last years in fields of micro machining. The main advantages of this technology are on the one hand the consistency of the process chain with a high level of design freedom [18, 19]. On the other hand, the use of laser equipped and automated 5-axis machine tools combined with a utilisation of the laser beam as an ‘optical tool’ with smallest diameters less than 25 µm, offer a lean process with a high stability.

The industrial manufacturing of complex shaped parts with functional, laser structured surfaces can be achieved with such systems. Laser surface structuring, based on the mechanism of material ablation, is substantially caused by a conversion of laser energy into heat and subsequent evaporation energy. The required high intensities are realised by using pulsed laser sources with pulse duration in the range of nanosecond or less and by focusing the laser beam to a spot diameter in micron range.

One of the main challenges using laser radiation as an invisible ‘tool’ for industrial manufacturing of filigree micro structures is to avoid thermal effects on the remaining base material. If the time period for the interaction between laser radiation and base material is too long, i.e. in the range of hundred picoseconds or longer, heat formation and conduction lead to significant melt phase formation [20]. The melting can cause material oxidation or changes the material structure like the formation of a white layer known from the electro discharging machining of steel [17]. Therefore, the so called ultra-short pulse laser sources with pulse durations in the range of single pico- and femtoseconds have entered the industrial field of production since a few years [18]. The main advantage of the use of these laser sources is an almost melt-free material ablation process, basing on non-linear effects inside the irradiated material at atomic scale during the absorption of laser energy. As a result of these effects vaporization is predominant during the process and melt formation is negligible.

With such an ultra-short pulse laser, first demonstrators for investigations regarding the wetting and passive fluid transport were machined (Fig. 5 and 6).

3 CONCLUSION

Wetting tests performed on laser structured surfaces showed a similar fluid spreading and transportation behaviour like that on the natural skin. In both cases the liquid spreads over parts of the surface and is later transported in capillary channels. For technical surfaces, hot working tool steel and cutting oil were used exemplarily for metal and oil as one of the most important material-liquid combinations in the field of mechanical engineering.

Hence, it is shown that a transfer of functional skin structures to technical materials with comparable wetting and transportation properties is possible. With specific transportation patterns of moisture harvesting lizards in mind, one can improve the derived functional structures regarding aspects of surface wettability and transportation.

4 EXPERIMENTAL

4.1 Analysis of biological model

Photographic images of the lizards were taken with a Canon EOS 350D (Canon Inc., Japan) with either the original telephoto lens or a 50 mm macro lens. The auto exposure setting was used without flashlight.

For SEM-imaging, tissue samples (approx. 1 × 3 mm) from different body regions of alcohol fixed museum specimen (Zoological Research Museum Alexander Koenig (ZFMK), Bonn) of the investigated lizards were taken. These samples were fixed overnight in 4% (v/v) glutardialdehyde in 70% ethanol followed by dehydration in an ascending alcohol series (90%, 60 min; 96%, 60 min; 99.8%, 60 min twice; 100%, 2 days). After washing three times for 20 minutes with hexamethyldisilazane, samples were dried at room temperature for 3 days. The samples were sputter-coated without further treatment with gold and observed using a Stereoscan S604 SEM (Cambridge Instruments, UK). Images were digitally recorded with an attached i-scan digitizer (ISS Group Services Ltd., UK) with an image acquisition time of 50 seconds.

For determination of the skin's wetting behaviour two different approaches were used. Scales were dissected from alcohol fixed museum specimen (ZFMK). Pictures of the meniscus arising from contact with deionised water were taken photographically (Canon EOS 350D, Canon Inc., Japan) with a 50 mm macro lens. Alternatively, droplets of 4-7 µl of deionised water containing 1% (w/v) blue food colour (Queen Fine Foods Pty. Ltd., Australia) were applied to the integument and spreading was observed with a digital high-speed microscope (Keyence VW-9000, Keyence Deutschland GmbH, Germany) at 125fps.

For histological analysis of the integument, samples of approximately 1 × 3 mm size were fixed in 70% ethanol containing 2% (v/v) glutardialdehyde and 2% (v/v) formaldehyde. The samples were dehydrated in an ascending alcohol series (3 × 15 min 70%; 15 min, 80%; 15 min, 90%; 15 min 96% and 3 × 30 min, 100%). The samples were put into LR-White resin (London Resin Company Ltd., UK) at 4° C overnight. The resin was changed to new LR-White and allowed to polymerise at 60° C for 48 hours. The samples were cut to 0.75 µm thick slices using an OM U3 microtom (Reichert, Austria), stained with Methylene Blue and investigated with a standard optical microscope.

4.2 Laser structuring (fabrication and parameters)

Micro structure patterns were designed with the CAD-software Siemens NX7.5 and also the matching with the surface of the CAD part model was performed in NX7.5. In the next step the CAD data was transferred into the CAM-software "FlexOStruk" developed by the Fraunhofer IPT to calculate the machine- and laser tool paths. For tool path calculation the distance between two single laser tool paths was set as a fix value of 10 µm.

The parts for machining were flat plates (50 x 50 x 10 mm) of hot working tool steel 38XCr-MoV5-1, tempered and quenched to a hardness of 52 HRC. To prove the feasibility of the defined surface, scale patterns were defined according to the abstracted structure information of the lizard skin. To prove possible scaling, dimensions were 1:1 (minimal lateral distance 50.0 µm) and 6:1 (minimal lateral distance 300.0 µm).

The laser surface structuring was performed on a 5-axis laser machine tool. In this machine, a Lumera picosecond laser 'SuperRapid' with a maximal laser average power of 9 W (at 80 kHz pulse repetition frequency) at a wave length of 532 nm was installed. For beam guidance a laser scanning unit 'intelliScan10' and a dynamic beam expander 'VarioScan20i' (both Scanlab AG) were installed, as well as for beam focusing a Linos telecentric f-theta-Ronar lens with a focal length of 100 mm, optimized for the laser wave length. With this optical setup, a focal spot diameter of 20 µm with Gaussian energy distribution profile was realized on the part surface. The laser average power was set to 4 W at 200 kHz and the feed rate of 500 mm per second.

The laser structured plates, especially their surface topography, were analyzed with a 3D-microscope Alicona Infinite Focus G4.

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REFERENCES

[1] Sherbrooke, W.C., Rain-harvesting in the Lizard, *Phrynosoma cornutum*: Behavior and Integumental Morphology. *Journal of Herpetology,* **24(3)**, pp. 302–308, 1990. doi: http://dx.doi.org/10.2307/1564398

[2] Peterson, C.C., Rain-harvesting behavior by a free-ranging desert horned lizard (*Phrynosoma platyrhinos*). *Southwestern Naturalist,* **43**, pp. 391–394, 1998.

[3] Vesely, M. & Modry, D., Rain-Harvesting Behavior in Agamid Lizards (*Trapelus*). *Journal of Herpetology,* **36(2)**, pp. 311–314, 2002. doi: http://dx.doi.org/10.2307/1566009

[4] Schwenk, K. & Greene, H.W., Water Collection and Drinking in *Phrynocephalus helioscopus*: A Possible Condensation Mechanism. *Journal of Herpetology,* **21(2)**, pp. 134–139, 1987. doi: http://dx.doi.org/10.2307/1564473

[5] Peterson, J.A., The Microstructure of the Scale Surface in Iguanid Lizards. *Journal of Herpetology,* **18(4)**, pp. 437–467, 1984. doi: http://dx.doi.org/10.2307/1564106

[6] Comanns, P., Effertz, C., Hischen, F., Staudt, K., Böhme, W. & Baumgartner, W., Moisture harvesting and water transport through specialized micro-structures on the integument of lizards. *Beilstein J. Nanotechnol.*, **2**, pp. 204–214, 2011. doi: http://dx.doi.org/10.3762/bjnano.2.24

[7] Sherbrooke, W.C., Scardino, A.J., de Nys, R. & Schwarzkopf, L., Functional morphology of scale hinges used to transport water: convergent drinking adaptations in desert lizards (*Moloch horridus* and *Phrynosoma cornutum*). *Zoomorphology,* **126**, pp. 89–102, 2007. doi: http://dx.doi.org/10.1007/s00435-007-0031-7

[8] Sherbrooke, W.C., Integumental water movement and rate of water ingestion during rain harvesting in the Texas horned lizard, *Phrynosoma cornutum*. *Amphibia-Reptilia* **25**, pp. 29–39, 2004. doi: http://dx.doi.org/10.1163/156853804322992814

[9] Withers, P., Cutaneous Water Acquisition by the Thorny Devil (*Moloch horridus*: Agamidae). *Journal of Herpetology,* **27(3)**, pp. 265–270, 1993. doi: http://dx.doi.org/10.2307/1565146

[10] Gans, C., Merlin, R. & Blumer, W.F.C., The Water-collecting Mechanism of *Moloch horridus* Re-examined. *Amphibia-Reptilia,* **3**, pp. 57–64, 1982. doi: http://dx.doi.org/10.1163/156853882x00167

[11] Bentley, P.J. & Blumer, W.F.C., Uptake of Water by the Lizard, *Moloch horridus*. *Nature,* **4829**, pp. 699–700, 1962. doi: http://dx.doi.org/10.1038/194699a0

[12] Hancock, M.J., Sekeroglu, K. & Demirel, M.C., Bioinspired Directional Surfaces for Adhesion, Wetting, and Transport. *Adv. Funct. Mater.*, **22**, pp. 2223–2234, 2012. doi: http://dx.doi.org/10.1002/adfm.201103017

[13] Stenzel,V, Wilke, Y. & Hage, W., Drag-reducing paints for the reduction of fuel consumption in aviation and shipping. *Progress in Organic Coatings,* **70**, pp. 224–229, 2011. doi: http://dx.doi.org/10.1016/j.porgcoat.2010.09.026

[14] Büttner, C. & Schulz, U., Shark skin inspired riblet structures as aerodynamically optimized high temperature coatings for blades of aeroengines. *Smart Materials and Structures*, **20(9)**, pp. 1–9, 2011. doi: http://dx.doi.org/10.1088/0964-1726/20/9/094016

[15] Gennes, P.G., Brochard–Wyart, F. & Quéré, D., *Capillary and wetting phenomena*. Springer-Verlag: Berlin and New York, 2010. doi: http://dx.doi.org/10.1007/978-0-387-21656-0

[16] Xin, B. & Hao, J., Reversibly switchable wettability. *Chem. Soc. Rev.*, **39**, pp. 769–782, 2010. doi: http://dx.doi.org/10.1039/b913622c

[17] Klocke, F., Funkenerosives Abtragen (Chapter 2), F*ertigungsverfahren 3 – Abtragen, Generieren und Lasermaterialbearbeitung*. 4th edition, Springer-Verlag: Berlin, pp. 3–126, 2007. doi: http://dx.doi.org/10.1007/978-3-540-48954-2_2

[18] Klocke, F., Arntz, K., Mescheder, H. & Winands, K., Reproduzierbare Designoberflaechen im Werkzeugbau. wt Werkstattstechnik online **99(11/12)**, pp. 844–850, 2009.

[19] Kordt, M., Konturnahes Laserstrahlstrukturieren für Kunststoffspritzgießwerkzeuge. PhD-thesis, RWTH-Aachen, 2007.

[20] Poprawe, R., Laser Application Technology (Chapter 15). *Tailored Light 2*, Springer-Verlag: Berlin and Heidelberg, pp. 343–357, 2011.