

Accepted Manuscript

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PII: S0927-7757(17)30627-1
DOI: <http://dx.doi.org/doi:10.1016/j.colsurfa.2017.06.065>
Reference: COLSUA 21752

To appear in: *Colloids and Surfaces A: Physicochem. Eng. Aspects*

Received date: 7-5-2017
Revised date: 22-6-2017
Accepted date: 23-6-2017

Please cite this article as: M.Gürsoy, M.T.Harris, A.Carletto, A.E.Yaprak, M.Karaman, J.P.S.Badyal, Bioinspired Asymmetric-Anisotropic (Directional) Fog Harvesting Based on the Arid Climate Plant *Eremopyrum orientale*, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*<http://dx.doi.org/10.1016/j.colsurfa.2017.06.065>

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Bioinspired Asymmetric-Anisotropic (Directional) Fog Harvesting Based on the Arid Climate Plant *Eremopyrum orientale*

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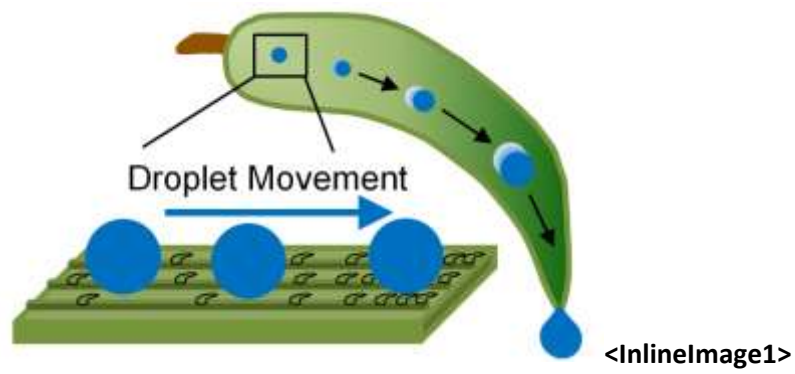
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HIGHLIGHTS

- *Eremopyrum orientale* plant leaf surface channels fog collection.

GRAPHICAL ABSTRACT



ABSTRACT

Asymmetric-anisotropic (directional) fog collection behaviour is observed for leaves of the arid climate plant species *Eremopyrum orientale*. This is underpinned by a hierarchical surface structure comprising macroscale grooves, microscale tilted cones (in the direction of water flow), and nanoscale platelets. Soft lithography combined with either nanocoating deposition or functional nanoimprinting has been used to replicate this highly-efficient directional water collection mechanism.

Keywords: Fog harvesting; water collection; bioinspired; hierarchical length-scales; *Eremopyrum orientale*; functional nanoimprinting.

- Hierarchical leaf surface structure comprises grooves, tilted cones, and nanotexture.
- Directional fog collection behaviour is replicated using functional nanoimprinting.

1. INTRODUCTION

The asymmetric-directional flow of liquids along surfaces has a wide range of potential applications including microfluidics, lab-on-a-chip, sensors, microreactors, lubrication¹, inkjet printing², heat exchangers^{3,4}. Asymmetric-anisotropic structures for such directional liquid flow have previously been observed in nature for shark skin denticles with ridges (riblets) which are understood to reduce drag when aligned parallel to the direction of water flow⁵, and butterfly wings, where nano-lamella are superimposed onto overlapping micro-scales causing water droplets to roll outwards radially⁶. In each of these cases, it is the oriented regular macro-scale structures which underpin the directional flow of water (with micro-scale grooves superimposed).

In this article, we describe the discovery of asymmetric-anisotropic fog collection behaviour for leaves of the *Eremopyrum orientale* plant species, which is found in arid climates such as North Africa, Southern Europe, South Western and Central Asia⁷. Such mechanisms for water harvesting from the air are important in relation to the development of cheap and environmentally-sustainable approaches for the supply of potable water for drinking and agricultural purposes in arid regions of the world^{8,9,10,11}. Other reported fog collectors found in nature include spindle-knots of spider silk¹², barbed surfaces of *Hordeum vulgare*¹³, cactus¹⁴, twisted spiral desert geophytes,¹⁵ and fibrous hairs of the *Cotula fallax* and *Salsola crassa* plant species^{16,17}. The gradient multi-length-scale surface structures of *Eremopyrum orientale* plant leaves have been successfully replicated in order to mimic the observed high efficiency asymmetric-anisotropic (directional) fog collection behaviour by either applying a hydrophobic nanocoating onto soft lithography replicas or using functional-nanoimprinting (which combines both physical replication and surface chemical functionalisation within the same soft lithography step¹⁸), Scheme 1.

2. EXPERIMENTAL

2.1 Plant Species

Eremopyrum orientale plant leaves were obtained during the growing season (April) from near Lake Bolluk, located in Cihanbeyli-Konya, Turkey.

2.2 Replication

Plant leaves were rinsed with water to remove any surface debris and allowed to dry in air. Negative moulds of these surfaces were prepared by application of a polyvinylsiloxane base and cure mixture (President Plus Jet Light Body, Coltene/Whaledent AG) to the substrate,^{19,20} and immediately pressing down using a glass slide for a cure period of 10 min. Once the negative mould had hardened, it was carefully peeled away from the natural substrate surface, rinsed with water, and left to dry. Positive replicas from the negative moulds were prepared using epoxy resin (epoxy resin L and hardener S, R&G Faserverbundwerkstoffe GmbH). The epoxy resin was thoroughly mixed in a 5:2 ratio of resin to hardener, and then poured over the negative mould. Any trapped air bubbles were removed by placing under vacuum, and then the mixture was left to cure for 36 h in a desiccator. Finally, the negative moulds were gently peeled away to reveal the positive replica of the *Eremopyrum orientale* plant leaf.

Initiated chemical vapour deposition (iCVD) of hydrophobic surface nanocoatings was undertaken in a custom-built stainless steel chamber (20 cm width, 30 cm length, and 5 cm height)²¹. The chamber was connected to a two-stage rotary pump, with a butterfly-valve (MKS) located between the chamber and the pump, which was used to control the chamber pressure

(monitored by a capacitance Baratron pressure transducer, MKS). This was achieved through a proportional–integral–derivative (PID) control unit (MKS), connected to both the pressure transducer and the butterfly-valve. Monomer 1H,1H,2H,2H-perfluorodecyl acrylate (PFDA, +97%, Sigma Aldrich) and initiator di-tertbutyl peroxide (TBPO, +98%, Sigma Aldrich) were used as received, without further purification²². Each substrate sample was placed inside onto the base of the chamber (maintained at 35 °C using water cooling), followed by evacuation to system base pressure. Next, precursor and initiator were vaporised inside stainless steel vessels connected to the chamber via needle control valves at predetermined pressures. A tungsten (+99.95%, 0.375 mm diameter, Alfa Aesar) filament array located 20 mm above the substrate surface was resistively heated using a variable transformer to initiate the polymerization reaction. Filament temperature during deposition was monitored using a K-type thermocouple (Omega) directly attached to one of the filaments. Depositions onto a reference silicon wafer were monitored by interferometry using a 632.8 nm He-Ne laser source. The deposition conditions used were as follows: 150 mtorr chamber pressure, 280 °C filament temperature, 0.5 sccm PFDA flowrate, 0.8 sccm TBPO flowrate. Upon completion of iCVD, the precursor feed valves were closed, and the chamber vented to atmosphere. 50 nm thickness nanocoatings were used.

In the case of cure activated nanolayer transfer, a functional coating was plasma deposited onto the negative mould prior to the filling with epoxy resin to produce the positive replica. Pulsed plasma deposition of the low surface energy precursor, 1H, 1H, 2H, 2H-perfluorooctyl acrylate (+95%, Fluorochem Ltd, purified using several freeze-pump-thaw cycles) was carried out in an electrodeless cylindrical glass reactor (5 cm diameter, 520 cm³ volume, base pressure of 1×10^{-3} mbar, and with a leak rate better than 1.8×10^{-9} kg s⁻¹) enclosed in a Faraday cage²³. The chamber was fitted with a gas inlet, a Pirani pressure gauge, a 30 L min⁻¹ two-stage rotary pump attached to a liquid cold trap, and an externally wound copper coil (4 mm diameter, 9 turns, spanning 8–15 cm from the precursor inlet). All joints were grease-free. An L-C network was used to match the output impedance of a 13.56 MHz radio frequency (RF) power generator to the partially ionised gas load. The RF power source was triggered by a signal generator, and the pulse shape monitored with an oscilloscope. Prior to each experiment, the chamber was cleaned by scrubbing with detergent, rinsing in water and propan-2-ol, followed by oven drying. The system was then reassembled and evacuated. Further cleaning consisted of running an air plasma at 0.2 mbar pressure and 50 W power for 30 min. Next, polyvinylsiloxane negative moulds, and reference silicon (100) wafer pieces (Silicon Valley Microelectronics Inc.) were inserted into the centre of the reactor, and the system pumped back down to base pressure. At this stage, 1H,1H,2H,2H-perfluorooctyl acrylate monomer vapour was introduced at a pressure of 0.2 mbar for 5 min prior to ignition of the pulsed electrical discharge. The optimum conditions for functional group retention corresponded to a peak power of 40 W, and a duty cycle on-time of 20 μ s and off-time equal to 20 ms. Deposition was allowed to proceed for 150 s to yield 58 ± 5 nm thick layers²⁴. Upon plasma extinction, the precursor vapour continued to pass through the system for a further 3 min, and then the chamber was evacuated back down to base pressure.

2.3 Characterisation

Photographs were taken using a camera (model Fujifilm FinePix S2950, Fujifilm Holdings, Japan). For higher magnification surface topography images, individual leaf specimens were prepared for scanning electron microscopy analysis by using a glycerol substitution process.²⁵ These were fixed overnight using 25% glutaraldehyde (Sigma-Aldrich Co.) in phosphate buffer solution (pH 7.2, Sigma-Aldrich Co.). Next, 2–4 mL of 2% glutaraldehyde solution was dispensed onto a small (~ 2 cm²) piece of fabric placed in a petri dish, and a leaf was placed on top of the soaked fabric for 2 h. The fabric was then replaced with a new piece, and it was soaked with a solution of 10% glycerol (>99%, Sigma

Aldrich Ltd.) and left for 2 h. The same process was repeated for increasing concentrations of glycerol up to 90% in 10% steps. No gold coating was used for the leaf samples due to the conductive nature of the glycerol.²⁶ Surface topography images were taken on a scanning electron microscope (Model LS-10 scanning electron microscope, Zeiss) operating in a secondary electron detection mode, in conjunction with 20 kV accelerating voltage, and a working distance between 9–11 mm. The epoxy resin positive replica samples were mounted onto a carbon disk supported on an aluminum holder, and coated with a 5 nm gold layer (Model 108 sputter coating unit, Cressington Scientific Instruments Ltd) in order to avoid excess surface charging. Images were taken on a scanning electron microscope (Cambridge Stereoscan 240) operating in secondary electron detection mode, in conjunction with 8 kV accelerating voltage, and a working distance between 8–26 mm. Surface features were analysed using image analysis software (ImageJ, public domain, <http://rsbweb.nih.gov/ij/>).

Microlitre sessile drop contact angle analysis was carried out with a video capture system (Model OCA 50, DataPhysics Instruments GmbH) using 2 μL dispensation of deionised water (BS 3978 grade 1). Advancing and receding contact angles were measured by respectively increasing and decreasing the droplet size until the contact line was observed to move.²⁷ A 9 μL water droplet size was employed for tilt angle measurements.

Mist collection measurements were undertaken by mounting each sample above an 11 mm inner neck diameter, 25 cm^3 volumetric flask (ISOLAB Laborgeräte GmbH), positioned on top of a mass balance, Supplementary Material Figure S1. 0.5–6.0 μm mist droplets were generated using a 6 cm^3 chamber volume nebulizer (Freely Plus Model: V5002, Atılım Sağlık A.Ş.), with air flow rate of 10 L min^{-1} and 3.5 bar pressure delivering a water nebulisation rate of 0.4 $\text{cm}^3 \text{min}^{-1}$. These droplet sizes are comparable to meteorological fog²⁸. The distance between sample front and nebulizer was set to 4 cm. All experiments were performed at 23 °C and repeated at least three times for each substrate sample type.

3. RESULTS

3.1 Characterisation of Plant

3.1.1 Optical Microscopy

The *Eremopyrum orientale* plant grows to approximately 25 cm in height with leaves which are 5–8 cm long and approximately 1 cm wide, Figure 1. The adaxial and abaxial surfaces are dark green and green respectively.

3.1.2 Contact Angle

During fog episodes, water droplets coalesce and roll along the length of the leaf towards the underlying ground, Figure 1 and Figure 2. Of particular interest is that water droplets roll preferentially (asymmetric-anisotropic) along one direction towards the leaf tip (rather than the petiole). Both sides of the leaf display hydrophobicity, with the adaxial tip exhibiting the highest static water contact ($164 \pm 1^\circ$) and lowest hysteresis $5 \pm 1^\circ$ values (which is indicative of superhydrophobicity²⁹) when viewed parallel (along) the length of each leaf, Table 1 and Figure 3. A higher contact angle is measured when viewed parallel (along) versus perpendicular to the length of each leaf, which is consistent with anisotropic spreading along the leaf towards the tip. Measurement of the tilt angle for water droplets showed a preference to roll along the leaf towards the tip rather than perpendicular to the leaf axis, Supplementary Material Video S1 and Video S2.

Table 1: Water contact angle and tilt angle water at which droplet starts to roll along *Eremopyrum orientale* adaxial leaf surface near leaf tip and positive replicas viewed parallel (along) and perpendicular to the length of each leaf. 2 μL and 9 μL water droplet sizes were employed for contact and tilt angle measurements respectively.

Sample	Contact Angle / °								Tilt Angle / °	
	Parallel				Perpendicular				Towards	Towards
	Static	Advancing	Receding	Hysteresis	Static	Advancing	Receding	Hysteresis	Tip	Petiole
Leaf	164 ± 1	163 ± 1	157 ± 1	5 ± 1	148 ± 1	153 ± 1	145 ± 1	8 ± 1	22 ± 2	26 ± 2
Replica	132 ± 3	133 ± 2	94 ± 3	40 ± 4	70 ± 5	78 ± 4	35 ± 3	43 ± 4	Adhered [†]	Adhered [†]
iCVD replica	161 ± 2	162 ± 1	118 ± 5	43 ± 6	151 ± 1	153 ± 2	104 ± 4	49 ± 5	34 ± 2	38 ± 3
Functional nanoimprint replica	159 ± 3	161 ± 2	110 ± 3	52 ± 4	152 ± 3	154 ± 3	102 ± 3	53 ± 4	40 ± 4	43 ± 5

[†] The water droplet did not roll-off even when turned past 90°.

3.1.3 Scanning Electron Microscopy

A hierarchical structure is visible on the adaxial leaf surface at higher magnifications, Figure 4. There appears to be macro grooves running along the length of the leaf approximately $96 \pm 13 \mu\text{m}$ apart, and their raised edges are covered with tilted cone-like structures (with a base diameter of $20 \pm 7 \mu\text{m}$ leaning away from the petiole towards the leaf tip (direction of rolling water droplet movement). The density of these tilted cone-like structures increasing on moving along the leaf towards the tip, which mirrors the rise in hydrophobicity, Figure 5 and Figure 3 respectively. On the nanoscale, the whole surface (excluding cones) is covered with $147 \pm 31 \text{ nm}$ width and $890 \pm 169 \text{ nm}$ length plant wax platelets.

3.2 Bioinspired Replication

The *Eremopyrum orientale* plant leaf surface macro and micro scale physical structures were accurately replicated using soft lithography; however the nanoscale wax platelet definition was poor, which is consistent with the inherent limitation of this technique^{18,19}, and manifests in higher water contact angle hysteresis values, Figure 4 and Table 1. These unfunctionalised positive replicas displayed anisotropic spreading of water droplets along the grooves, (resulting in an asymmetric

shaped droplet) and enhanced directional mist collection, both of which follow the behaviour observed for the actual plant leaf surface, Table 1, Table 2, Figure 3, and Figure 6. Control experiments using flat polyethylene sheet and following iCVD perfluoroalkyl chain hydrophobic coating of flat polyethylene sheet showed no directional enhancement in water collection.

Table 2: Mist collections efficiencies between 60–120 min for *Eremopyrum orientale* adaxial leaf and bioinspired functional surfaces, see Supplementary Material Figure S2. Directional enhancement is defined as the increase in water collection efficiency for the leaf tip pointing downwards versus upwards.

Surface	Water Collection Efficiency / $\text{g m}^{-2} \text{h}^{-1}$		Directional Enhancement / %
	Tip Pointing Upwards	Tip Pointing Downwards	
Reference flat PE sample	58.8 ± 7.62	-----	0
Reference iCVD functionalised flat polyethylene sample	80.8 ± 2.7	-----	0
Leaf	104 ± 5.1	115.9 ± 2.2	11.6 ± 3.2
Unfunctionalised replica	90.8 ± 2.59	95.4 ± 1.0	5.1 ± 2.3
iCVD functionalised replica	106.9 ± 1.9	136.8 ± 7.8	27.9 ± 5.3
Functional nanoimprint replica	107.6 ± 3.15	129.2 ± 2.1	21.0 ± 4.4

In order to achieve the high levels of hydrophobicity and low directional tilt angles observed for the *Eremopyrum orientale* leaf surface, the positive replicas were functionalised with perfluoroalkyl chains using either iCVD or functional nanoimprinting techniques. This helps to address the lower Cassie-Baxter hydrophobicity arising from the inherent limitation of poor nanoscale plant wax platelet definition associated with the soft lithography technique^{18,19,30}. The obtained hydrophobic functionalised replica surfaces gave rise to asymmetric-anisotropic wetting enhancements far exceeding those associated with the unfunctionalised replica surface or the *Eremopyrum orientale* plant species, Figure 6, Table 1, and Table 2,.

4. DISCUSSION

Symmetric-anisotropic wetting of grooved plant leaf structures is known to give rise to either hydrophobicity or hydrophilicity depending upon the dimensional parameters employed^{31,32,33}. The key factor for such water flow is understood to be the grooves running parallel to the long axis of the adaxial leaf surface, which guide the downslide of droplets once they have grown in size to the point at which the gravitational weight exceeds any droplet attachment mechanism. Simple grooved

structures replicating such fog / water collection behaviour have previously been reported, although these do not provide enhanced forwards versus backwards (asymmetric) movement of water droplets along the grooves beyond 'downward with gravitational weight' effects^{3,32,34,35,36,37,38,39,40,41,42}. Such symmetric anisotropic droplet spreading along grooves for fabricated model surfaces display higher contact angles when viewed along the grooves versus perpendicular^{33,41,43,44,45,46,47,48,49,50}, which is consistent with the present study, Table 1. Furthermore, the superimposition of micro-textures onto grooves to create hierarchical surfaces enhances anisotropic wetting akin to what is observed for the *Eremopyrum orientale* plant leaves, Figure 4.
33,51,52,53,54

For the case of asymmetric-anisotropic wetting of surfaces, previous model studies undertaken in the laboratory demonstrate such behaviours through the creation of either chemical gradient wettabilities⁵⁵ or equally-spaced tilted pillars prepared by reactive-ion-etching⁵⁶. The accompanying theoretical model developed in the latter study, describes the criterion for directional liquid movement to be governed by the ability for droplet spreading to reach the next asymmetric surface protrusion⁵⁶. In the present investigation, we have found that such asymmetric-anisotropic wetting is also present in nature on the adaxial surfaces of *Eremopyrum orientale* plant leaves, which is attributed to a hierarchical combination of grooves running along the length of the leaf (approximately 100 μm apart), and decreasing (non-regular) spaced tilted cones (approximate base diameter 20 μm) pointing towards the leaf tip (direction of water flow). The density of these tilted cone-like features increasing towards the leaf tip, which mirrors the rise in hydrophobicity attributable to the Cassie-Baxter effect³⁰, Figure 5 and Figure 3 respectively. In addition, the whole surface (excluding cones) is covered with nanoscale plant leaf wax platelets which also enhance hydrophobicity also due to Cassie-Baxter behaviour³⁰. This should be contrasted with untilted regular spaced pyramidal (base 14 μm) hierarchical structures which do not display directional water collection⁵⁷ or anisotropic chemically patterned surfaces⁵⁸. In terms of length scales, the physical structures present on *Eremopyrum orientale* plant leaf surfaces are reversed when compared to previously reported oriented (tilted) macro-scale surface structures containing superimposed micro-scale grooves for shark skin⁵, butterfly wings⁶, or plant leaves⁵⁹.

These *Eremopyrum orientale* plant leaf surface structures have been replicated by using either soft-lithography (which is a well-proven method for the physical replication of plant leaf structures^{60-61,62,63}) or functional nanoimprinting (combines both physical replication and surface chemical functionalisation within the same soft lithography step¹⁸). The fabricated functionalised plant replica surfaces have shown enhanced levels of mist collection compared to corresponding flat surfaces which can be attributed to a combination of asymmetric-anisotropic wetting along the tilted cone containing grooved surfaces in association with hydrophobicity, Figure 6. Asymmetric-anisotropic wetting along these hierarchical surfaces encourages directional movement of the collected water droplets, whilst hydrophobicity (to mimic nanoscale plant leaf wax platelets) lowers water droplet adhesion to the surface.

Given that around one billion people in the world lack access to clean drinking water (with many living in arid or semi-arid regions⁶⁴) and three out of four jobs worldwide are water-dependent (stifling economic growth in developing countries⁶⁵), such enhancements for water collection efficiencies are highly desirable. Other potential applications include microfluidics, lab-on-a-chip, sensors, microreactors, lubrication, inkjet printing, and heat exchangers.

5. CONCLUSIONS

Eremopyrum orientale plant leaf surfaces display asymmetric-anisotropic (directional) mist collection behaviour which is underpinned by a hierarchical surface structure comprising macro-scale grooves, micro-scale cones (tilted in the direction of water flow), and superimposed nanotexture. The density of tilted cones increases on moving from the leaf petiole to tip. These surfaces have been replicated by using soft lithography combined with either nanocoating deposition or functional nanoimprinting, and shown to be highly-efficient for directional mist collection.

6. ACKNOWLEDGEMENTS

This work was supported by Engineering and Physical Sciences Research Council (EPSRC) grant reference EP/J005401/1. M. Gürsoy was supported by The Scientific and Technological Research Council of Turkey (TÜBİTAK) - BİDEB National Doctoral Fellowship Program. We thank R. Fraser for carrying out thickness measurements.

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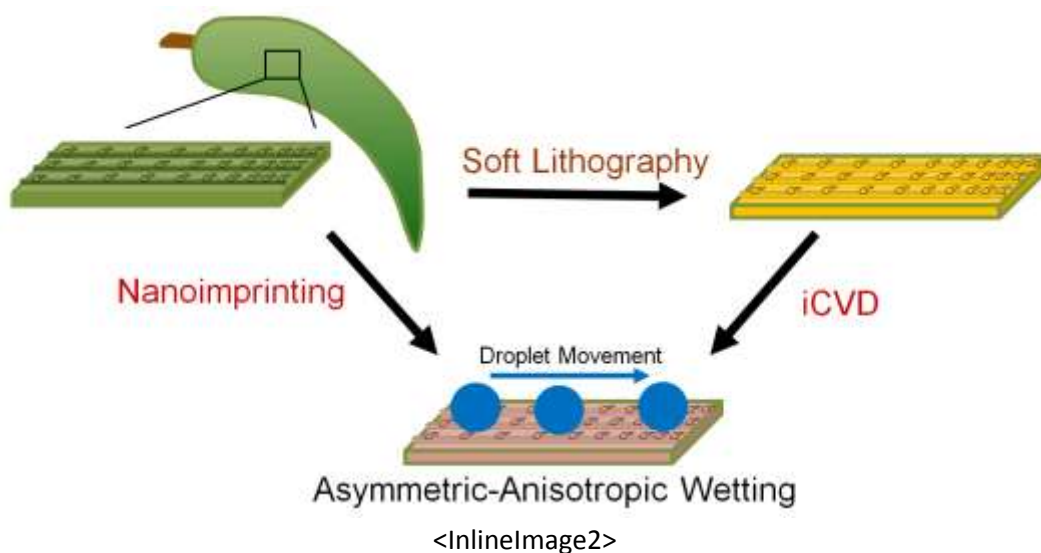
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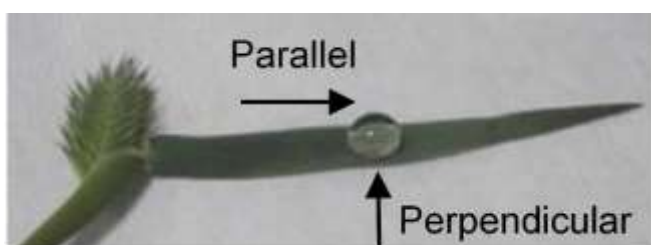


Scheme 1: Replication of *Eremopyrum orientale* plant leaf surface.

(a)



(b)



(c)

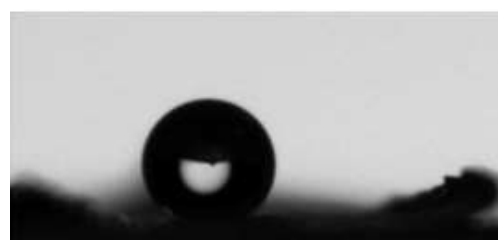


Figure 1: Photographs of *Eremopyrum orientale* plant species taken in April during the growing season: (a) whole plant; (b) large water droplet placed on middle of adaxial surface; and (c) small water droplet placed near leaf tip of adaxial surface viewed along (parallel to) leaf axis from petiole towards tip ($164 \pm 1^\circ$ static water contact angle).

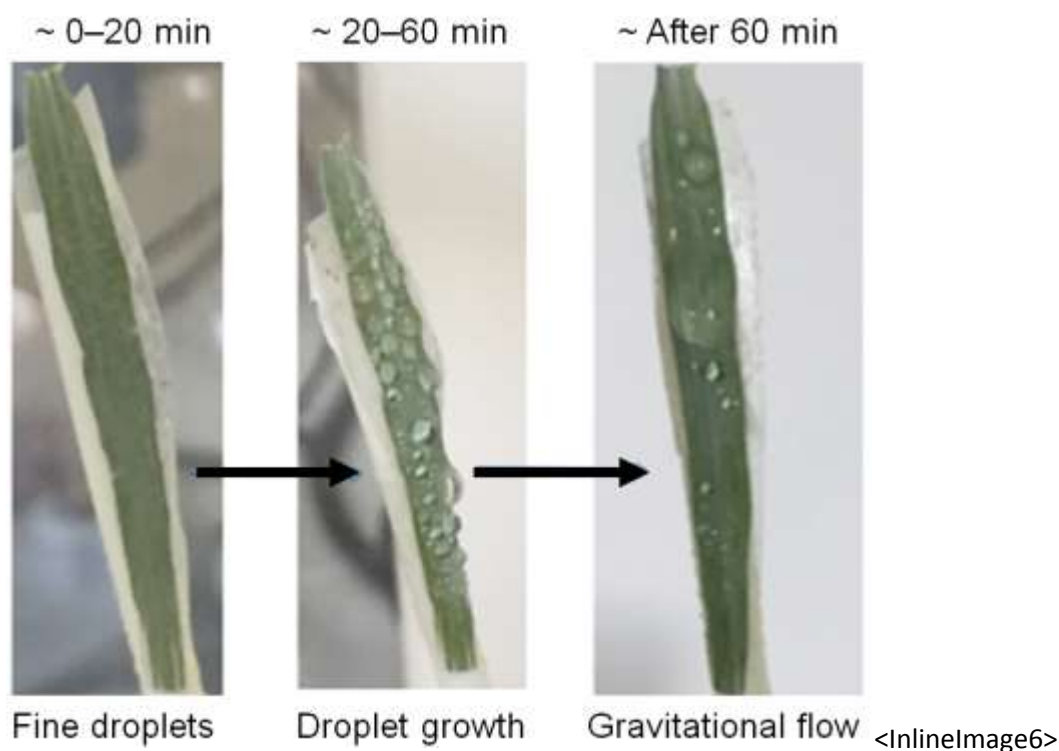


Figure 2: Mist collection on *Eremopyrum orientale* adaxial leaf surface over time (the white edges are paper used to support the leaf). Width of leaf is approximately 1 cm.

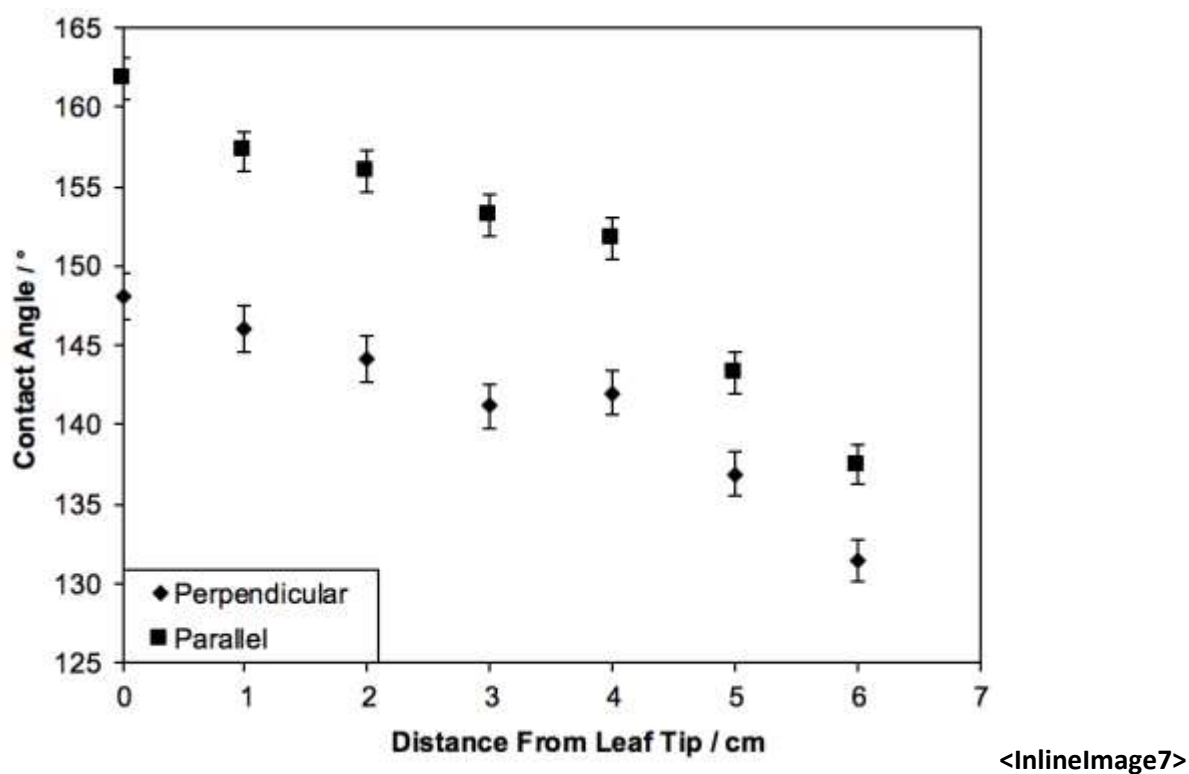


Figure 3: Water contact angle values viewed parallel (along) and perpendicular to the length of *Eremopyrum orientale* plant adaxial leaf surface as a function of longitudinal distance from the leaf tip (total length 6 cm).

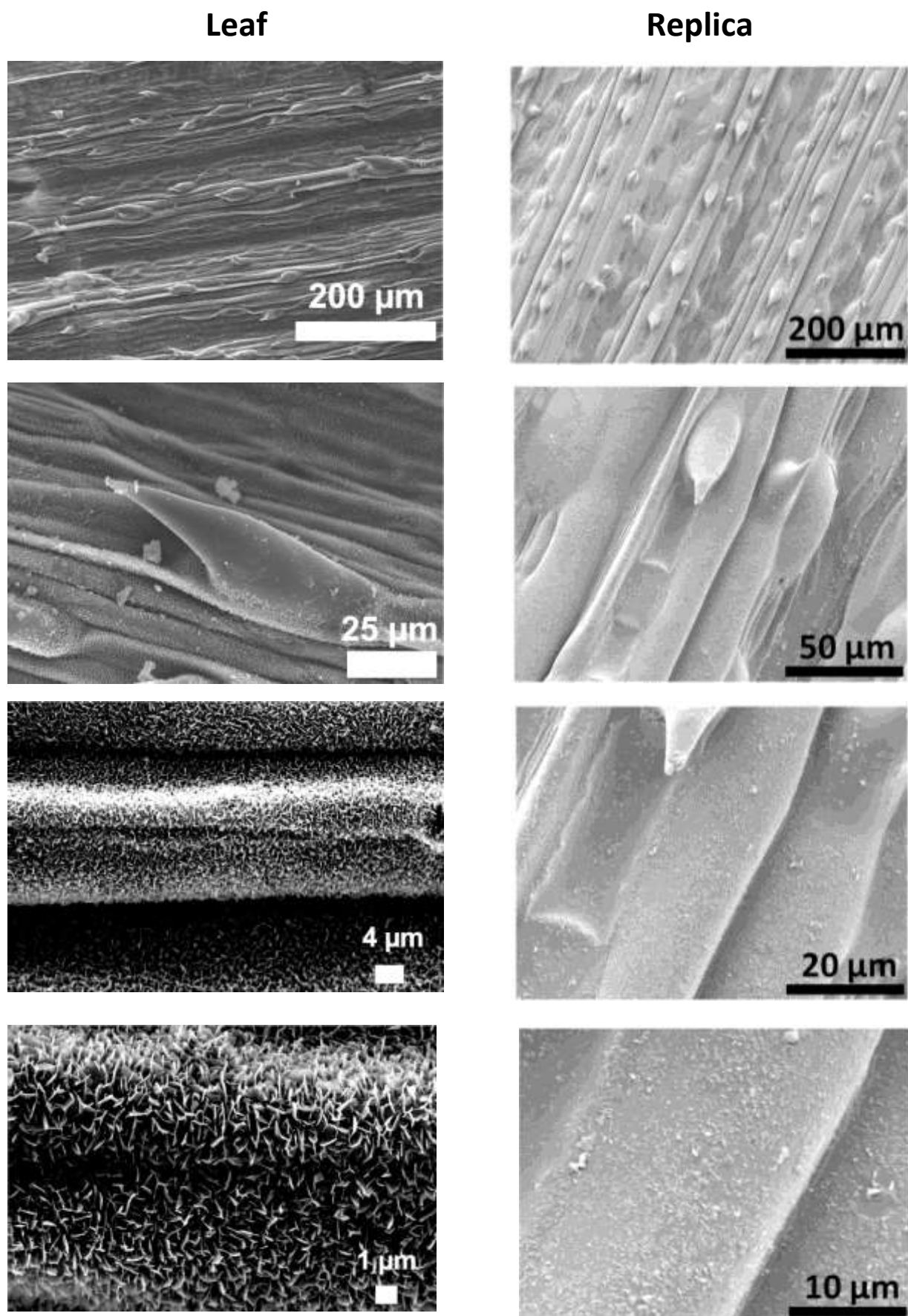


Figure 4: SEM images of *Eremopyrum orientale* adaxial leaf middle region and replica.

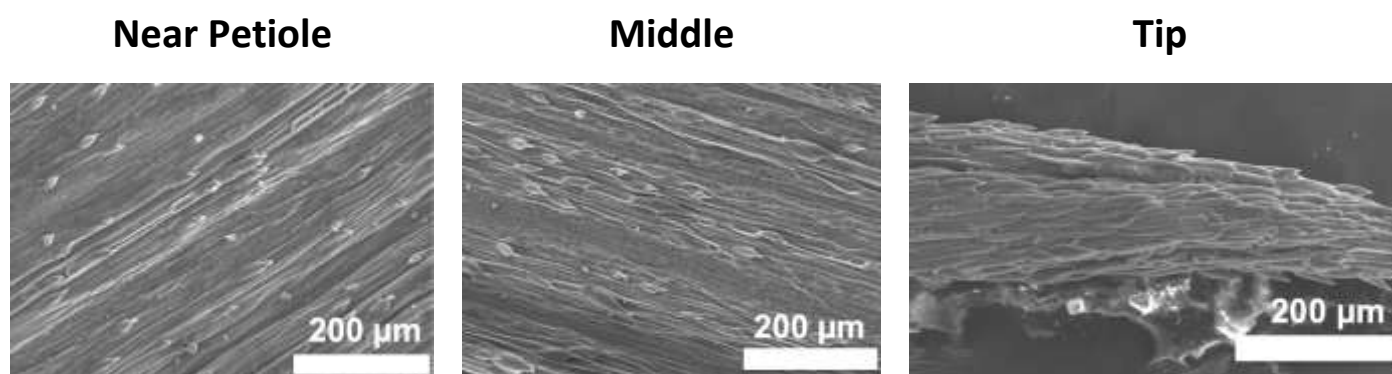


Figure 5: SEM images taken along the length of *Eremopyrum orientale* adaxial leaf showing cones pointing towards tip (left to right).

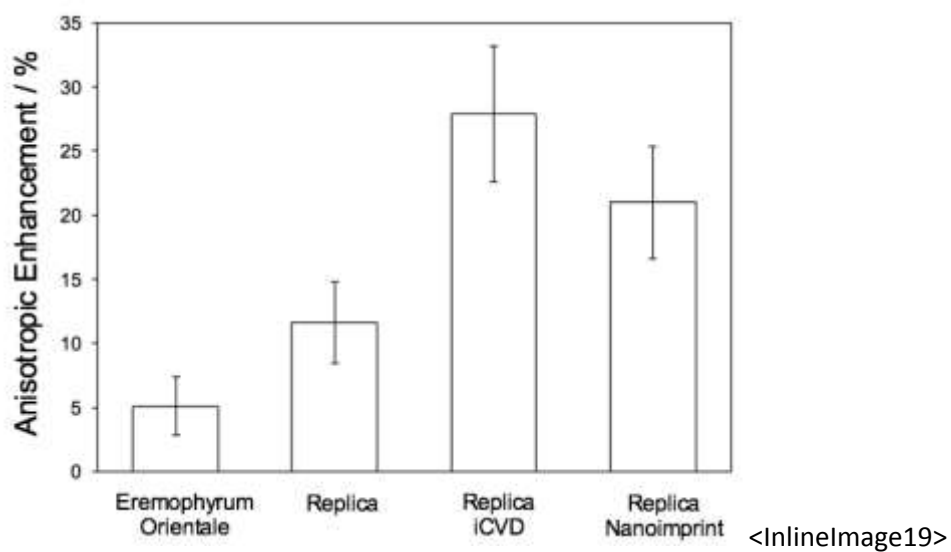


Figure 6: Anisotropic (directional) enhancement of steady state mist collection efficiencies for micro-scale tilted cones pointing vertically downwards versus upwards for *Eremophyrum orientale* adaxial leaf, unfunctionalised replica, iCVD functionalised replica, and functional nanoimprint replica, see Supplementary Material Figure S2.