Supporting Information

Directional shedding-off of water on natural/bio-mimetic taper-ratchet array surfaces

Peng Guo¹, Yongmei Zheng¹*, Chengcheng Liu¹, Jie Ju² and Lei Jiang^{1,2}

- Key Laboratory of Bio-Inspired Smart Interfacial Science and Technology of Ministry of Education, School of Chemistry and Environment, Beihang University Beijing 100191, P. R. China E-mail: zhengym@buaa.edu.cn
- 2. Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

Supplementary Figure Legends (Fig. S1-S7):

Figure S1. a) *Ryegrass* plant leaf is about 10 millimeter in width and about 100-200 millimeters in length, having better superhydrophobicity in natural environment. b) The larger water drop can usually be condensed on leaf surface, in the shape of elliptoid-sphere. The distinct striped structure is reflected, the directions is defined as 1, 2, 3 and 4 direction, respectively, indicated with yellow arrows, respectively. c-d) The static contact angle on fresh *ryegrass* leaf surface $\theta_{1/} = \sim 150^{\circ}$ along the 1 \leftrightarrow 2 direction (c); and along the $3\leftrightarrow$ 4 direction, contact angle $\theta_{\perp} = \sim 154^{\circ}$ (d). The $3\leftrightarrow$ 4 direction is vertical to the $1\leftrightarrow$ 2 direction.



Figure S2. The SEM images of the negative PDMS replica of leaf. a-c) The periodic pores can be resulted from the ratchet-structure on fresh leaf, were clearly shown; d) The negative structure of nano-scale crystalline can be in well agreement with the size of fresh leaf. Scale bars, a, 100 μ m; b, 50 μ m; c, 5 μ m; d, 500 nm.



Figure S3. SEM image of nanoparticles on micro-level taper-ratchet structure on PVDF polymer surface.



Figure S4. Observation on static contact angles on artificial periodic ratchet surface: a) $\theta_{//} = \sim 151^{\circ}$ along the 1 \leftrightarrow 2 direction; b) $\theta_{\perp} = \sim 156^{\circ}$ along the 3 \leftrightarrow 4 direction.



Figure S5 Observation on dynamic contact angles on artificial surfaces. **a)** In the $1\leftrightarrow 2$ direction, drop moves its mass-centre toward the 1 direction in advancing process with time (frames 1-3), the maximum advancing angle can be ~ 156° at 10.224 s and doesn't recover its mass-centre in receding process with time (frames 3-5), the minimum receding angle can be ~ 133° at 19.262 s. **b)** In the $3\leftrightarrow 4$ direction, the mass-centers of drops are symmetric in advancing and receding process with time (frame 1-5). The advancing and receding angles can be ~ 155° at the 10.224 s and ~ 154° at the 19.262 s, respectively.



- 26 -

Figure S6 The anisotropic rolling-off of drop on artificial polymer surface. a) In the 1 direction, drop rolls easily off, with the roll-off angle of less than 2° ; b) In the 2 direction, drop hardly rolls off, with the roll-off angle of more than 20° . The drop is 15 µL in volume.



Figure S7 The unidirectional rolling-off properties of drops on artificial polymer surfaces under vibrations. a) The surface is exerted by 50 Hz random vertical vibration, the drop jumps up and down and rolls off along the 1 direction (see arrows) and b) The surface is exerted by 50 Hz horizontal vibration, the drop rolls off along the 1 direction (see arrows). The drop is 10 μ l in volume. The processes are recorded by high-speed CCD camera.



Supplementary Information:

Analysis on asymmetric retention force

According to the Kawasakil^[28] and Furmidge^[29], a retention force can be balanced with the gravity of a drop for sliding-off the surface, i.e., can be described with

$$f = w \gamma (\cos\theta r - \cos\theta a) \tag{1}$$

where w is the width of drop toward the direction of drop moving, γ is the liquid surface tension. θ r is the receding angle of drop; θ a is the advancing angle of drop. It can be understood, in a complete wetting contact mode, the contact width for a rough surface is larger than that for a smooth surface. But in a composite contact mode, the rough geometry can trap much more air, so that the drop is suspended up by rough structure. The contact width can be complex in terms of the geometry.

An edge angle can fluctuate the solid-liquid interface, accordingly, changes the receding and advancing angle of a drop along the direction of drop motion. For a ratchet with triangle geometry, the left/right bottom angle is rise up to φ_L/φ_R . Thus the advancing angle $\theta_a = \theta_{a_0}+\varphi_i$, where φ_i is the rise angle; receding angle $\theta_r = \theta_{r_0}-\varphi_i$, which was described by Extrand ^[16], where, θ_{a_0} is the true advancing angle; θ_a is the apparent advancing angle; θ_{r_0} is the true receding angle; θ_r is the apparent receding angle. $\Delta \theta_0 = \theta_{a_0}-\theta_{r_0}$. The retention force f_i in i direction can be further described as:

$$f_{i} = w\gamma(\cos\theta r - \cos\theta a) = w\gamma(2\sin\frac{\theta r + \theta a}{2}\sin\frac{\theta a - \theta r}{2})$$
(2)

For the taper-ratchet structure, which is different from the usual ratchet and pillars, but tips of taper-ratchets are conical with apex angle and tilted up with tilted-up angle to base of leaf surface, and are oriented toward the one direction. So the tip of taper-ratchet modulates mainly the behavior of wetting in directions, changing advancing contact angle and receding contact angle of a drop in process of movement. According to the report by Hancock & colleagures^[7], we illustrate the behavior of liquid in the 1 and 2 direction (Fig. 4C-D). The advancing $\theta a_{1,2}$ and receding angles $\theta r_{1,2}$ can be described, respectively.

In the 2 direction, $\theta a_2 = \theta a_0 - \varepsilon$; $\theta r_2 = \pi - \theta r_0 - (\varepsilon + \delta)$ (Fig. 4C). From Eq. (2), the retetion force f_2 can be described as following:

$$f_2 \sim w_2 \gamma (\cos\theta r_2 - \cos\theta a_2) = w_2 \gamma \{ (2\sin(\frac{\theta r_0 + \theta a_0}{2} - \frac{\pi - \delta}{2}) \sin[\frac{\Delta \theta_0}{2} - (\varepsilon - \frac{\pi - \delta}{2})] \}$$
(3)

In the 1 direction, $\theta a_1 = \theta a_0 - \varepsilon$; $\theta r_1 = \theta r_0 + \varepsilon$ (Fig. 4D). From Eq. (2), the retetion force f_1 can be described as following:

$$f_1 \sim w_1 \gamma (\cos \theta r_1 - \cos \theta a_1) = w_1 \gamma [2 \sin \frac{\theta r_0 + \theta a_0}{2} \sin (\frac{\Delta \theta_0}{2} - \varepsilon)]$$
(4)

Where θ_{a0} is intrinsic advancing angle; θ_{10} is intrinsic receding angle, $\Delta \theta_0$ is difference of intrinsic advancing angle and intrinsic receding angle, i.e., $\Delta \theta_0 = \theta a_0 - \theta r_0$. Herein, we measure $\theta_{a0} = \sim 100^{\circ}$ and $\theta_{10} = \sim 55^{\circ}$ for smooth PVDF surface. The tip of taper-ratchet has tilted up angle $\varepsilon \sim 25^{\circ}$ and apex-angle $\delta \sim 5^{\circ}$. The w_{1,2} is the solid-liquid contact width, i.e., w_{1,2}=2 π R $\lambda_{1,2}$, where R is the appearent contact radii of a drop, $\lambda_{1,2}$ is linear solid fraction in the D1/D2 direction, $\lambda_{1,2}=w_{0(1,2)}/L$, among which w_{0(1,2)} is the diameter of tip of taper-ratchet dependence on direction, L is the periodicity of neighbouring stripes composed of taper-ratchets. Furthermore, w_{1,2}=k w_{0(1,2)} (k = 2π R/L, the proportion constant), due to the pinning mode, w₂ > w₁, so it is can be estimated, w₂/w₁ is ranged from the maximum 25 to the nimimum 1 (w_{0, max}=2.5 µm; w_{0, min}=0.1 µm). From Eq. (3) and (4), the ratio of f₂/f₁ is thereby estimated to up to 100 at maximum and 4 at minimum dependence on the contact depth with tip of taper-ratchet in alternative direction (i.e., 1 and 2 direction) for directional water shedding-off on as-fabricated artificial PVDF surface with taper-ratchets.