A simple strategy to realize biomimetic surfaces with controlled anisotropic wetting

Dong Wu,1 Qi-Dai Chen,1,a) Jia Yao,1 Yong-Chao Guan,1 Jian-Nan Wang,1 Li-Gang Niu,1 Hong-Hua Fang,1 and Hong-Bo Sun1,2,a)

1State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, 2699 Qianjin Street, Changchun 130012, People’s Republic of China
2College of Physics, Jilin University, 119 Jiefang Road, Changchun 130023, People’s Republic of China

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The study of anisotropic wetting has become one of the most important research areas in biomimicry. However, realization of controlled anisotropic surfaces remains challenging. Here we investigated anisotropic wetting on grooves with different linewidth, period, and height fabricated by laser interference lithography and found that the anisotropy strongly depended on the height. The anisotropy significantly increased from 9° to 48° when the height was changed from 100 nm to 1.3 μm. This was interpreted by a thermodynamic model as a consequence of the increase of free energy barriers versus the height increase. According to the relationship, controlled anisotropic surfaces were rapidly realized by adjusting the grooves’ height that was simply accomplished by changing the resin thickness. Finally, the perpendicular contact angle was further enhanced to 131° ± 2° by surface modification, which was very close to 135° ± 3° of a common grass leaf.

A wealth of surfaces in nature not only exhibit good hydrophobic ability but also behave directional wetting, such as the rice leaf,1 the wings of the butterfly,2 the trionum flower,3 the duck feather,4 and the shark skin.5 This phenomenon, crucial for the natural species surviving, is known as anisotropic wetting. It is considered that the directional arrangement of microstructures was the key reason for anisotropy. Surfaces with controlled anisotropic wetting restrict liquids flow to desired directions, and are expected to greatly improve the functions of, for example, microfluidic devices6,7 and evaporation-driven formation of nanopattern.8,9 The potential applications have attracted lasting research efforts.10–13 For example, Jiang et al.1 grew aligned carbon nanotubes to mimic the surface of a rice leaf; Morita et al.10 reported macroscopic anisotropy on line patterned surfaces of fluoroalkylsilane monolayers by vacuum ultraviolet lithography; Zhao et al.11 prepared sub-micrometer periodic grooved surface on azobenzene polymer films by laser interference. Despite of these exciting works, precisely controlling anisotropic wetting which is highly desired in practical applications6–9 remains challenging because of the lack of a systematic study and deep insight into physics of anisotropic wetting. Until now it is unclear how to control anisotropy and it is also unknown whether it is possible to develop a simple approach to realize controllable anisotropy. In addition, the anisotropy on submicrometer scale periodic grooves has been found weak, only about the magnitude of several micrometers. This agrees well with the theoretical results calculated by a thermodynamic model.17,18 With optimal parameters, artificial biomimetic surfaces with controlled anisotropy were realized.

Shown in Figs. 1(a) and 1(c) are bird-view scanning electron microscope (SEM) images of 2 μm period and 400 nm height grooves structures with different linewidths. The grooves with several micrometers period were the most common and useful structures for studying anisotropic wetting, here we also focused on this regime. Four kinds of grooves with widths from 600 to 1500 nm were obtained by controlling the laser exposure dosage. The exposure time was

![FIG. 1. (Color online) Anisotropic wetting on grooves with different line- widths and periods. (a) and (c) SEM images of 2 μm period and 400 nm height grooves structures with different linewidths. (b) and (d) the corresponding CA. (e) 2.5 μm period groove. (f) The CA measurement curve.](image-url)
much as 104°. The laser wavelength significantly cause the increase of FE barriers, which is in inset of Fig.2. However, it was noted that all the tension, it has to overcome the energy barrier exerted by the groove. When it spreads along the perpendicular direction, it became very long, as shown in Fig.2. Due to the strong anisotropy, the droplet along the groove was obtained when the grooves were illuminated under white light, just like the one of the Hibiscus trionum flowers.4

In order to better understand the physical mechanism of anisotropic wetting on the groove, a thermodynamic model18 was developed to calculate the change in the surface FE as a function of the instantaneous CA during the three-phase contact line moving along the two orthogonal directions. The wetting in our case is in the noncomposite state [the inset in Fig. 3(a)], where the water completely penetrates into the grooves, because the θ1 strongly depends on the height. The magnitude of the FE barriers increases as the groove height increases, which could lead to the increase in the degree of wetting anisotropy. For the model, provided that the droplet area was constant, an equation was deduced from geometrical analysis to calculate the θ from A to B

\[ \theta_A \times \frac{L_A^2}{\sin^2 \theta_A} - \frac{L_A^2}{\sin^2 \theta_B} \times \frac{\cos \theta_A}{\cos \theta_B} - \theta_B \times \frac{L_B^2}{\sin^2 \theta_B} \]

where the initial \( \theta_A \) is chosen as 150°, \( L_A \) is 1 mm, \( L_B = L_A + a \) and \( \theta_B \) is the CA for the flat surface. Then, the relative FE barrier for AB and BC section18 was calculated and the whole FE barrier curve was obtained.

The FE barrier with respect to CA for groove with 1.3 μm height was calculated, as shown in Fig. 3(a). The F was normalized with respect to the surface tension \( r_{LV} \) between liquid and gas state and the FE unit will be mm. From the FE barrier curve, we see that there are a minimum FE at 101°, which means the equilibrium state for the water droplet on the grooved surface because the least energy state is the most stable for a system. The experimental value 104° ± 2° agreed well with the theoretical result. The calculation method, the FE barrier for the previous 400 nm height groove was obtained. The equilibrium CA was about 72°, which was very close to the measured value 76° ± 2°. The small difference ∼4° was partially caused by the measurement error. In addition, the groove shape we assumed in

FIG. 2. (Color online) Strongly anisotropic wetting on a 1.3 μm-height groove and its optical properties. (a) 45° tilted-view SEM image of the groove. The inset is the AFM measurement. (b) the corresponding CA. (c) A camera photo of the groove sample with ten grooved regions. (d) An iridescent diffraction pattern of the groove. The inset is the AFM measurement.
Numerical analysis was square,\(^{17,18}\) which had small error compared with the actual cross section of groove. This also affected the difference of anisotropy. To further investigate the relationship between the height and the anisotropy, groove structures with different heights, e.g., 200, 600, and 1000 nm were prepared, and the measured CA's [Fig. 3(b)] were in accordance with the theoretical results. It was evidently seen that the anisotropy strongly depended on the groove height. This made it possible for us to precisely control the degree of the anisotropy by changing the groove height.

To verify this possibility, we freely selected certain angle, for example, 90°. Along the curve in Fig. 3(b), we deduced that the groove height was about 800 nm. Then, by controlling the thickness of the resin, 800 nm height groove [Fig. 4(c)] was realized and the measured CA was 90° ± 2°, just as what we expected. To further verify the possibility of realizing controlled anisotropy, a smaller anisotropy, e.g., 65° would be obtained when the height was around 100 nm according to theoretical analysis. Experimentally, the measured CA on 100 nm-height groove surface [Fig. 4(a)] was about 64° ± 2° [Fig. 4(b)]. The anisotropy was only 9°, which was very close to the results reported by Zhao et al.\(^{11}\) They obtained the degree of the anisotropy 9.8° when the height was 127 nm. According to our studies, we deduce that the weak anisotropy on submicrometer grooves\(^{11}\) is mainly caused by the small height (<150 nm). Likewise, the reason for the weak anisotropy wetting on the line-patterned surface of fluoralkylsilane monolayer (∼100 nm) reported by Morita et al.\(^{10}\) is also the small height.

For most natural anisotropic surfaces, the CAs along both of the parallel and perpendicular directions are very large (>120°) because larger CA is beneficial for water to roll down. For example, the \(\theta_1\) and \(\theta_2\) are about 135° ± 3° and 120° ± 2° [the insets in Figs. 5(a) and 5(b)] for a common grass leaf. From the SEM images [Figs. 5(a) and 5(b)], we can find that the surface microstructures are in directional arrangement [the white arrow in Fig. 5(a)]. Although the \(\Delta \theta\) is only 15°, it is enough for living species to control the water movement direction. For our grooved surface, in order to increase both of the \(\theta_1\) and \(\theta_2\), we adopted low-surface-energy fluoralkylsilane\(^{10,20}\) to modify the 1.3 \(\mu\)m height groove. After surface modification, the \(\theta_1\) was increased from 104° ± 2° [Fig. 2(b)] to 131° ± 2° [Fig. 5(c)] and \(\theta_2\) was enhanced from 56° ± 1° [the inset of Fig. 2(b)] to 108° ± 1° [Fig. 5(d)]. This result was very close to the theoretical \(\theta_1\) 135° by the FE barrier calculation.

In conclusion, anisotropic wetting behaviors on groove structures with different parameters were systematically studied. Specially, we found the strongly dependence between the anisotropy and the height. Then, we proposed to precisely control anisotropy by adjusting the grooves’ height. This method was very simple and easily realized by laser interference lithography. Finally, the CAs were enhanced by surface modification and the wetting property of artificial grooved surfaces was more close to those natural anisotropic surfaces. These results not only provide new insights into the anisotropic wetting phenomenon but also are beneficial to freely design anisotropic surfaces for bioinspired system application.

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