Surfaces with Deterministically Fabricated Gradient Nanostructures for Spatially Varying Wettability

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Surfaces with spatially varying wettability provide gradient surface tension. Apart from being used as a "library" to investigate the interfacial phenomena [1], it also induces a driving force to droplets on the surface without extra power supply. It has found applications in biomedicine [2], microfluidics [3] and water collection [4] areas. However, deterministic fabrication of long-lifetime, large-area, reproducible gradient wetting surface remains a big challenge. In this work, deterministic and ordered large-area concentric gradient nanostructures, which are fabricated using interference lithography, are adopted to achieve the gradient wettability (Figure 1a). The concentric gradient structures gradually change from pillars to holes from center to edge (Figure 1 b ~ d) and are transferred from photoresist into cyclic olefin copolymer (COC) film by UV-NIL and thermal-NIL. In addition, to investigate how nanostructures affect the water wetting behaviors, the local water contact angle was characterized as a function of positions on COC film with concentric gradient nanostructures and we also established a numerical model to link the varied nanostructures with apparent water contact angles.

The images of water droplets on various positions are shown in Figure 2 a ~ h with images of corresponding underlying nanostructures. The quantitative measurement results of static water contact angle are shown in Figure 2i. As the position getting far away from the center, the contact angle first gradually increased from 108.1° to 132.1° from center to the position at 8 mm with the gradually increasing pillar diameter, and then decreased to 102.9° at 14 mm due to the increasing filling ratio and decreasing hole diameter. The water contact angle reaches the maximum at position 8 mm where the filling ratio is around 50%.

To establish a linkage between nanostructures and the water contact angle to further understand the water droplet wetting behavior on nanostructures, two classic models, the Wenzel model and the Cassie model, and two models of the intermediate states, are investigated (Figure 3a). Immersion depth and grooves filling ratio are critical parameters in the intermediate state 1 and 2, respectively. With theoretical calculation shown in Figure 3 b ~ d, we conclude that in the nanopillar region, water wetting behavior has an intermediate state in which some grooves are fully wetting while the rest are completely non-wetting. With the increasing of pillar diameter, the water filling ratio decreases. This work sheds light on liquid wetting behaviors at the nanoscale, and will promote the development of large-area fabrication methods for deterministic non-uniform structures which can be applied in biomedicine, microfluidics, plasmonic sensing, etc.

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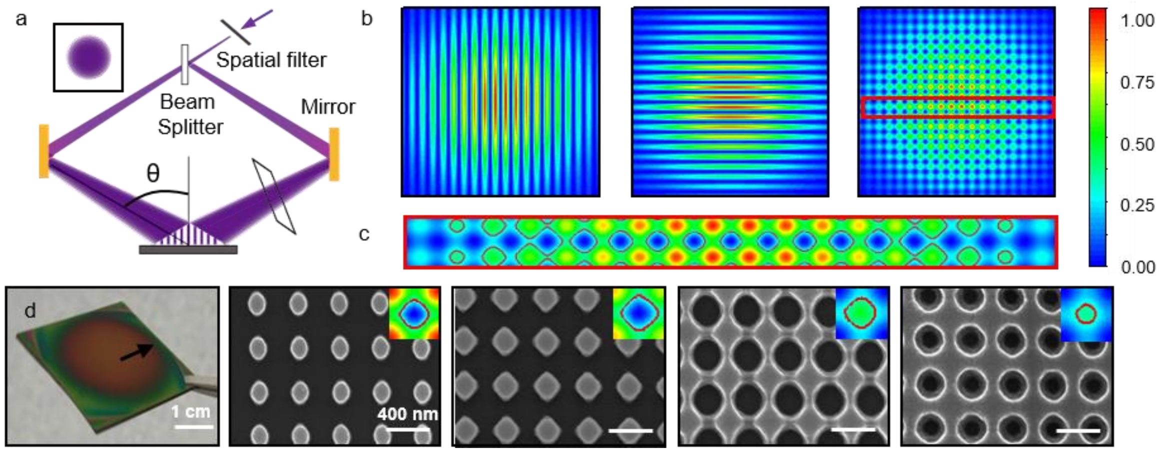

Figure 1. Fabrication of gradient nanostructure by interference lithography. (a) Schematic of interference lithography principle. (b)~(c) Simulation result of normalized light intensity distribution. (d) The sample after double interference lithography patterning and its SEM images at different positions.

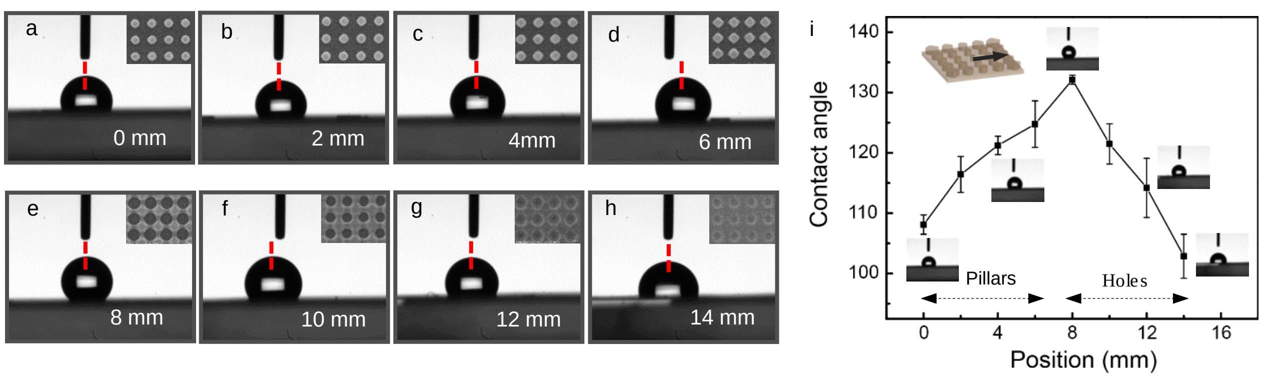

Figure 2. Varying water contact angle on gradient nanostructures. (a) ~ (h) Optical images of water droplets on different positions of gradient COC pattern (0 mm ~14 mm from the center), insets are SEM images of corresponding nanostructures. (i) Water contact angle at corresponding positions of (a) ~ (h).

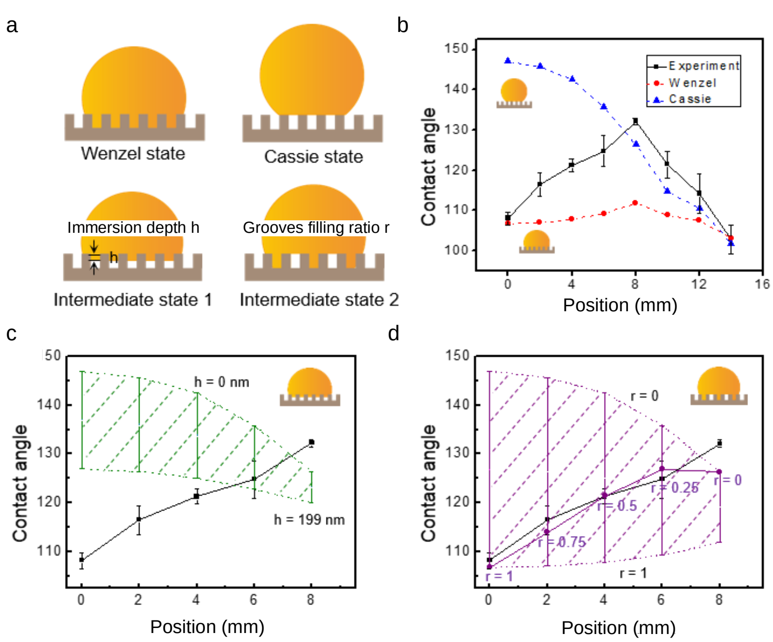

Figure 3. Modeling of water wetting behaviors over gradient nanostructures. (a) Schematic illustration of two classic wetting models and two intermediate state models. (b) Contact angle on different positions of COC film with gradient nanostructures from experiment and theoretical calculation of Wenzel model and Cassie model. (c) and (d) The comparison of experimental contact angle and theoretical calculated possible range of intermediate state 1 and 2 (The green and purple dash line area).