Superhydrophobic Tracks for Low-Friction, Guided Transport of Water Droplets

*Henrikki Mertaniemi, Ville Jokinen, Lauri Sainiemi, Sami Franssila, Abraham Marmur, Olli Ikkala, and Robin H. A. Ras**

Surfaces that are non-wetting to water, i.e., superhydrophobic,[1–4] are of considerable interest for scientists and engineers, not only for fundamental research, but also for the numerous attractive features including self-cleaning and non-wetting fabrics,[5] anti-fogging,[6] anti-icing,[7] buoyancy[8] and drag reduction.[9] By definition, a surface is superhydrophobic if the contact angle between a water drop and the surface at the solid/liquid/air interface is larger than 150°, and the contact angle hysteresis is small, i.e., drops readily slide or roll off when the surface is tilted slightly.[10–12] Here we explore the feasibility of using superhydrophobicity for guided transport of water droplets. We demonstrate a simple yet efficient approach for droplet transport, in which the droplet is moving on a superhydrophobic surface, using gravity or electrostatic forces as the driving force for droplet transportation and using tracks with vertical walls as gravitational potential barriers to design trajectories. Although the slope of the platform is as small as a few degrees, the drops move at a considerable speed up to 14 cm s^{-1}, even in highly curved trajectories. We further demonstrate splitting of a droplet using a superhydrophobic knife and drop-size selection using superhydrophobic tracks. These concepts may find applications in droplet microfluidics and lab-on-a-chip systems where single droplets with potential analytes are manipulated.[13–16]

There are two factors required for obtaining a superhydrophobic surface. First, the surface must have suitable roughness. Second, the surface must have a hydrophobic surface chemistry.[17,18] If these requirements are fulfilled, a water drop applied to the surface can adopt the Cassie wetting state where air remains trapped in microscopic grooves under the drop – a necessary condition for superhydrophobicity.[10] We prepared two different types of superhydrophobic tracks, ones having a bottom and others bottomless, on different substrates. Tracks with a bottom were made by milling of shallow grooves into copper plates. Tracks without a bottom were cut entirely through the substrate and were made in zinc plates by laser cutting, or to silicon wafers by etching. The metal tracks in copper and zinc were made superhydrophobic by galvanic deposition of silver followed by deposition of a fluorinated thiol surfactant.[19] The silicon tracks were made superhydrophobic by nanograss generated by plasma etching followed by a plasma deposition of fluoropolymer,[20] and had advancing and receding contact angle of 170 ± 2°. The superhydrophobic copper surface had advancing and receding contact angles of respectively 166 ± 2° and 164 ± 2°, whereas zinc had respectively 168 ± 2° and 166 ± 4°. The contact angle hysteresis was a few degrees maximum, which enabled drops to easily slide on the surface. The superhydrophobicity of the metal surface was observed to prevent the drop from entirely entering a track, even when a track had no bottom, as seen in **Figure 1**a,b, which shows photographs of a drop in superhydrophobic tracks with and without a bottom. Drop shapes are deformed by gravity to adapt to the shape of the track, while the superhydrophobicity prevents wetting of the metal surface. It can be observed that the weight of the drop is partially supported by the bottom of the 0.3 mm deep track.

Drops are able to move in the superhydrophobic track when the metal plate is tilted slightly, here to an angle of about two degrees. Without tracks, a drop moves in a straight trajectory as it follows the gravity gradient. However, in case of the superhydrophobic surface with tracks, the drops move along the track. A plate with a tortuous track containing curves of various radii is illustrated in Figure 1c. Drop movement in a curve is precisely guided by the track, as shown by a series of images in Figure 1e. A drop can be guided through many subsequent curves, provided that it does not have too high a velocity. A series of images with drops passing through multiple curves is shown in Figure 1g. The original video is available in Supporting Information (Video S1).

Miniaturization of the tracks is possible using lithography methods on silicon substrates. A drop in a miniaturized track with a width of 500 μm is shown in Figure 1f, and the corresponding video is in Supporting Information (Video S2). Much smaller tracks, down to 100 μm, were also fabricated, but these could not be tested due to difficulties in manually producing small enough droplets. Tracks with very small widths would be suited for systems with an automatic dispensing system capable of producing sub-microliter droplets.

In addition to gravity, also electrostatic force can be utilized to move drops on a superhydrophobic surface. A water drop in a

H. Mertaniemi, Prof. O. Ikkala, Dr. R. H. A. Ras
Molecular Materials
Department of Applied Physics
Aalto University (formerly Helsinki University of Technology)
Puumiehenkuja 2, FI-02150 Espoo, Finland
E-mail: robin.ras@aalto.fi, Homepage: http://tfy.tkk.fi/molmat/
V. Jokinen, Prof. S. Franssila
Department of Materials Science and Engineering
Aalto University (formerly Helsinki University of Technology)
Vuorimiehentie 2, FI-02150 Espoo, Finland
Dr. L. Sainiemi
Division of Pharmaceutical Chemistry
University of Helsinki
Viikinkaari 5E, FI-00790 Helsinki, Finland
Prof. A. Marmur
Department of Chemical Engineering
Technion – Israel Institute of Technology
32000 Haifa, Israel

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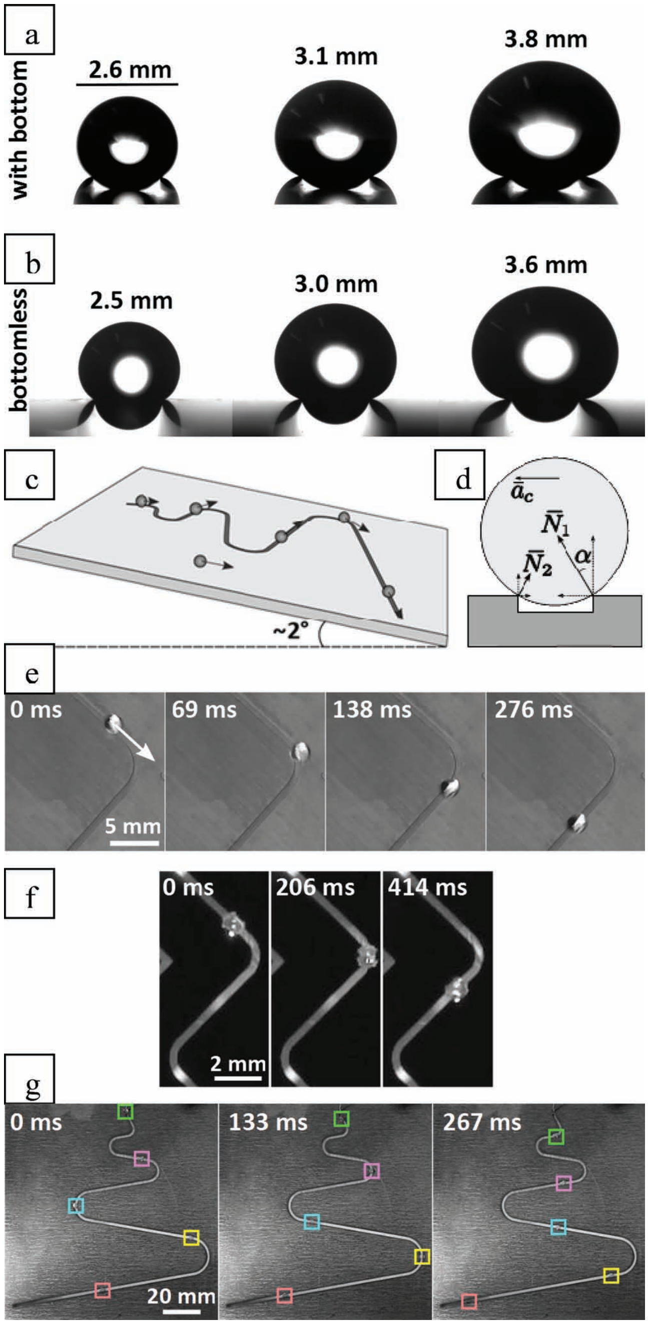

Figure 1. a) Images of water drops in a superhydrophobic track with a depth of 0.3 mm and a width of 1.6 mm. b) Water drops in a superhydrophobic track without a bottom. Track width 1.6 mm. c) The drop is able to roll at very small tilt angles. A drop outside the track moves in a straight line in the direction of gravitational gradient, while the path of drops in the curved track is precisely guided by the track. d) Normal forces acting on a hard solid sphere in a track. e) A sequence of images showing a 10 μL drop guided by a superhydrophobic copper track. Track width 1 mm. f) A 0.9 μL drop moving on a miniaturized track in silicon prepared by lithography methods. Track width is 0.5 mm. See Video S2. g) Guided transport of water droplets in a track with many curves (drop volume is 20 μL). Track width is 1.5 mm. For clarity, drops have been marked with boxes via image editing. See Video S1.

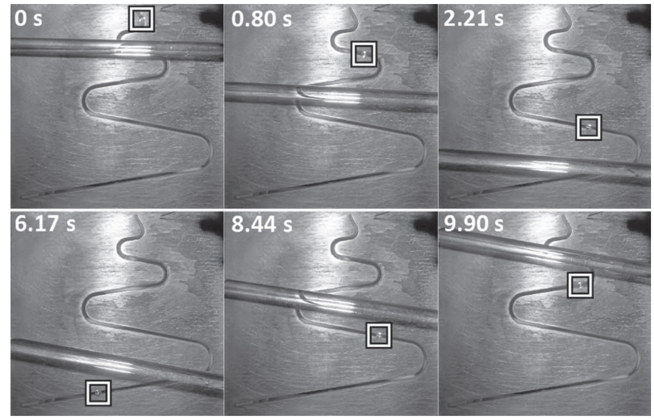

Figure 2. Electrostatic actuation of drop movement on a horizontal surface. A charged glass rod is employed for providing the electrostatic force for moving the water drop. The path of the drop is precisely guided by the superhydrophobic track. For clarity, the drop has been marked with a box via image editing. See also Video S3.

superhydrophobic track is attracted by a charged object, thus enabling the drop to be moved by moving the charged object. Electrostatic actuation of drop movement is shown in **Figure 2**, where a glass rod with static charges is utilized for moving a water drop in a superhydrophobic track on a horizontal plate. The path of the drop is precisely guided by the superhydrophobic track. The original video is available in the Supporting Information (Video S3).

The motion of a drop in a track can be quantitatively compared to the motion of an ideal hard sphere, taking into account that the situation for a drop is more complex as liquids deform and are affected by surface tension forces. An ideal hard sphere moving in a curved track is pressed down by gravity and supported by normal forces from the track edges as shown in Figure 1d. For a sphere in a constant curvature track, there is a maximum velocity at which the sphere is still able to pass the curve. The velocity $v_{\max}$ is related to the track radius of curvature R by $v_{\max}^2 = Rg\tan\alpha$ where the relationship between the angle α, the track width, s, and the sphere diameter, d, is $\sin\alpha = s/d$. These equations give a value for $v_{\max}$ of 0.213 m s^{-1} for a hard sphere with a diameter of 3 mm in a track with a width of 1.5 mm and a radius of curvature of 8 mm. In comparison, the maximum velocity of a water droplet, 3 mm in diameter, in a similar bottomless track, was experimentally found to be 0.143 ± 0.004 m s^{-1}. This gives a ratio of squared velocities $v_{\max,\text{experimental}}^2 / v_{\max,\text{hardsphere}}^2 = 0.45 \pm 0.02$. The reduced value in case of the water droplet is likely due to deformations induced by the track edge to the droplet. As the direction of the droplet is changed by the curved track, the center of mass of the drop is shifted towards the outer edge of the track, thus causing droplets to fail the curve at velocities lower than for ideal hard spheres.

For enabling more complex trajectories, we demonstrate that two tracks can intersect in junctions and crossings. In **Figure 3**a, two drops moving through a junction of two tracks is shown. Using junctions, drops from two or more locations are routed to one destination. Crossings, like the one shown in Figure 3b, would enable pathways to be designed with fewer spatial constraints (see also Video S4 in Supporting Information).

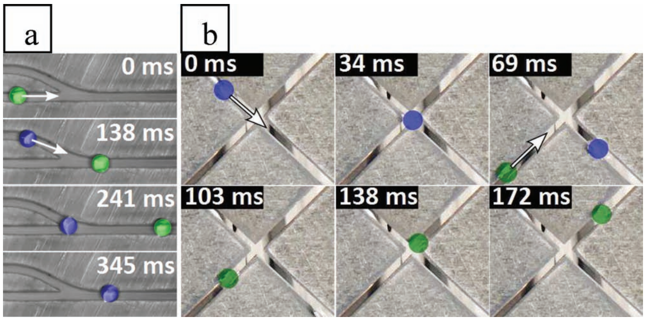

Figure 3. Two types of intersections. a) A series of images showing a junction of two tracks. Track width 1.5 mm. b) A series of images showing a crossing of two tracks. Track widths 1.2 mm (before crossing) and 1.5 mm (after). Drops have been colored via image editing for clarity. See Video S4.

The superhydrophobic tracks also enable manipulation of droplets as shown in the following two examples. First, we demonstrate that using a bottomless track with varying width, one can differentiate between drop sizes. Drops with a diameter smaller than the track width are not supported anymore by the track walls and fall through the track (**Figure 4**a,b and Video S5 in Supporting Information). A local widening of the track thus permits a large droplet to continue on the track, while a small droplet falls through the track. Second, some applications require that drops are cut into smaller droplets. This has been reported using devices based on electrowetting or surface forces.[16,20,21] Here we present a different approach using a superhydrophobic knife. A sharp superhydrophobic blade, inserted between and equidistant from the sides of the track, is able to effectively cleave an incoming water droplet to form two smaller droplets. (Figure 4c,d and Video S6 in supporting information). Splitting was observed if the drop had sufficiently high kinetic energy compared to its surface energy. If the velocity was too low, drops were observed to rebound from the blade without splitting. A systematic quantitative investigation of the energy required for drop splitting is planned to be the topic for another study.

In conclusion, we demonstrate a new, simple and general approach for transportation of water droplets based on superhydrophobic technology. Water droplets are transported at high velocity in tracks that are made superhydrophobic to ensure low friction. The track walls provide confinement of the drop trajectory to the track. Junctions and crossings enable complex pathways for the drops. Manipulation of droplets is demonstrated including size-selection using a local widening in the track and splitting of water droplets using a superhydrophobic knife. We foresee that this technology for drop transport could open up new directions to low-cost microfluidic applications that, in contrast to most current drop transport technology, do not rely on electric power. In addition, combining suitable track geometry to a computer-controlled electric field or tilting stage would enable the programming of complex trajectories for droplets.

Experimental Section

Superhydrophobic tracks in metal: Superhydrophobic tracks were prepared on metal plates with a size of about 120 × 120 mm. Track geometries were designed using Autodesk AutoCAD software. Tracks were cut to copper plates by milling (Protoshop Oy) and to zinc plates by laser cutting (CO_2 laser, wavelength 10.6 µm; Multilaser Oy). Milling enabled having tracks with a bottom, and laser cutting resulted in tracks without a bottom (Figure 1a,b). Tracks in copper had a depth of 0.3 mm and constant widths ranging from 1 to 1.6 mm, whereas tracks in zinc had constant or varying widths ranging from 1 to 1.9 mm. Zinc plates with a thickness of 1.5 mm were used. Subsequent to track cutting, a superhydrophobic coating was applied to the metal plates. First, the plates were polished with sandpaper (P600). Second, the plates were washed with ethanol and acetone. Subsequently, the superhydrophobic coating was applied employing the procedure by Larmour et al.[19] First, the metal plate was immersed in a silver nitrate solution (0.010 mol dm^{-3}), to produce a silver microstructure by electroless galvanic deposition. Thereafter, the metal plate was immersed in a solution of 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol in CH_2Cl_2 (1 mmol dm^{-3}). Silver nitrate (99%, Riedel-de Haën) and 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (97%, Aldrich) were used as received.

Superhydrophobic tracks in silicon: Tracks that had widths of 100 µm, 200 µm and 500 µm were fabricated on 500 µm thick single crystalline silicon wafers using deep reactive ion etching (DRIE) (Plasmalab System 100, Oxford Instruments, Bristol, UK). First, the tracks were etched through the wafer using DRIE and aluminum etch mask. Then, aluminum was removed in phosphoric acid and the second DRIE step formed silicon nanograss (a.k.a. black silicon) on the wafer.[20,22] Finally, the nanograss was made superhydrophobic by coating with a thin layer of fluoropolymer in CHF_3 plasma.[20,22]

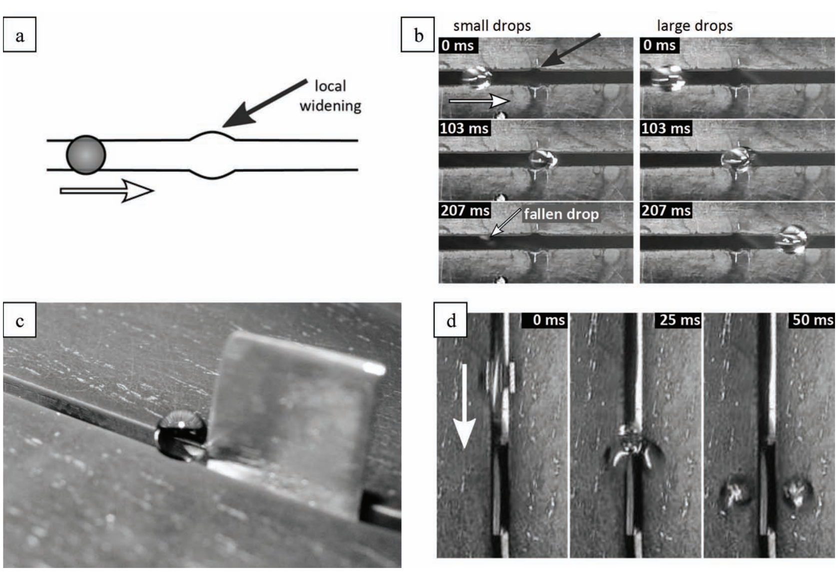

Figure 4. a,b) Droplet size selection. A track with a local widening can be used to select between different drop sizes. Images captured from Video S5 demonstrate the selecting between drop sizes. Small drops fall through a local widening in the track, whereas large drops continue on the track. c,d) A superhydrophobic knife can be used to split a drop into two. The sequence of images captured from Video S6 demonstrates the splitting of a drop. Track width 1.5 mm.

Contact angle measurements: Contact angles were measured at 4–5 spots on the surface, using a KSV Instruments CAM 200 contact angle measuring device with a software-controlled dispenser. A 25-gauge flat-tipped needle was used and the water was purified with a Milli-Q system. KSV bundled software was used to fit Young-Laplace curves to images for determining contact angles. Averaged values of a 6 μL drop are reported.

Drop generation: For applying multiple subsequent drops to a superhydrophobic track, a flat-tipped needle was connected to a 50-cm plastic tube filled with water. For experiments with curved tracks, a 25-gauge needle was used, and a 14-gauge needle for drop-splitting experiments. The hydrostatic pressure of the water inside the vertical tube resulted in a flow with a relatively constant drop rate from the needle.

Superhydrophobic knife: One edge of a copper plate with a thickness of 0.5 mm was sharpened using a file. Subsequently, a superhydrophobic coating was applied as described above for metal plates employing the procedure by Larmour et al.[19]

Glass rod with static charges: A glass rod was electrostatically charged by rubbing with a nitrile glove and operated manually to actuate drop movement on a horizontal plate.

High-speed video recording: For recording videos, a Casio EX-FH25 digital camera was used. Videos were analyzed using ImageJ software.

Supporting Information

Six movies (Video S1 to S6) are available as Supporting Information from Wiley Online Library or from the author.

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